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YOKELSON,
R.J.

FINAL REPORT FOR RESEARCH AGREEMENT
INT-95009-RJVA
"Analysis of Trace Gasses Using Opticial Remote Sensing"
UNIVERSITY OF MONTANA
FS Contact: Dr. Darold E. Ward
CoOp Contact: Dr. Geoffrey N. Richards

Analysis of Trace Gases Using Optical Remote Sensing

Final Report: INT95009-RJVA

To:
USDA Forest Service
Intermountain Research Station
Intermountain Fire Sciences Laboratory
Missoula, MT 59807

By:

Robert J. Yokelson
Associate Research Professor, Department of Chemistry, University of Montana

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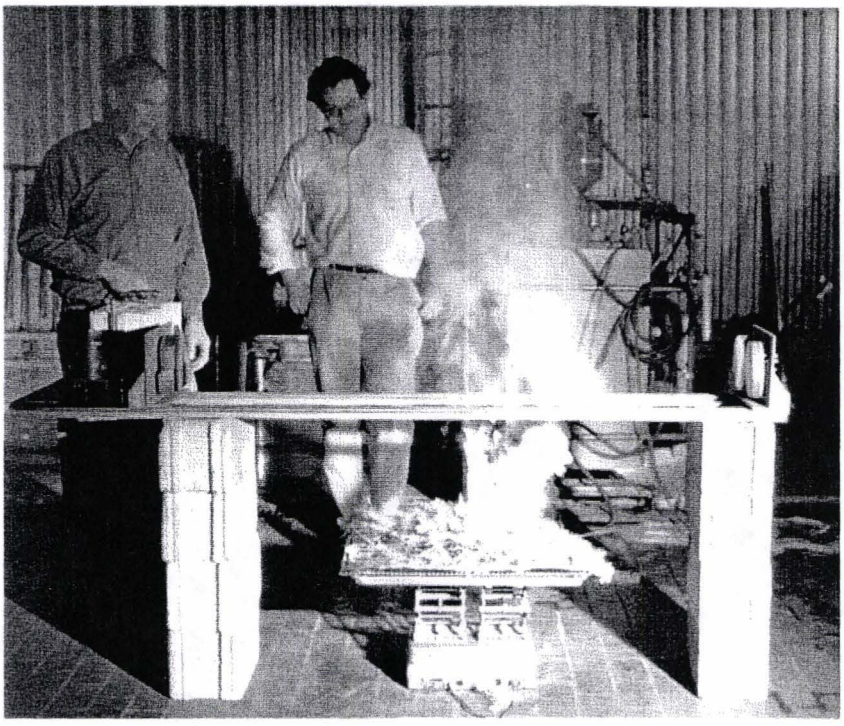

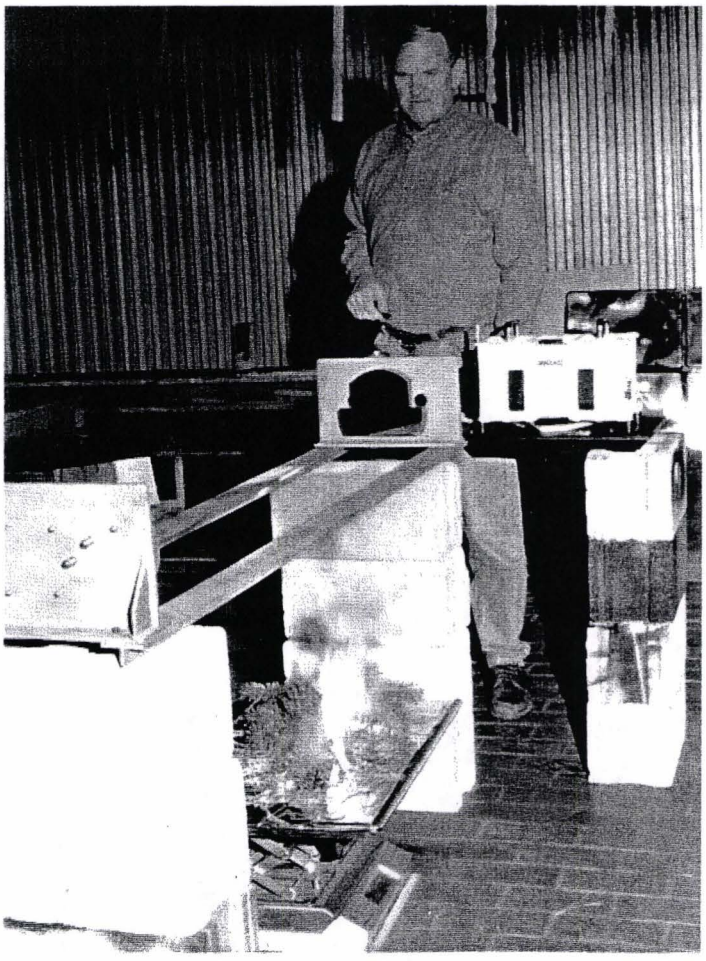

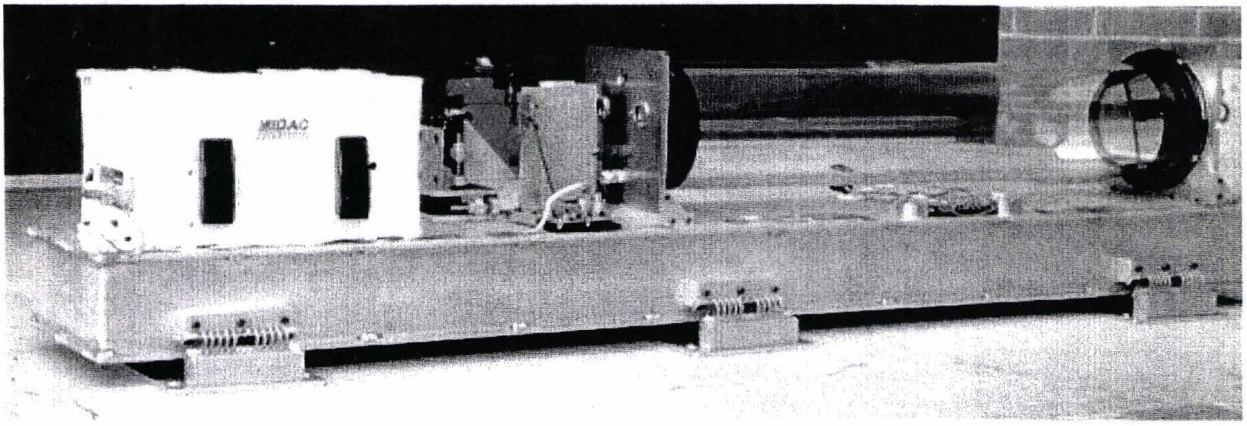

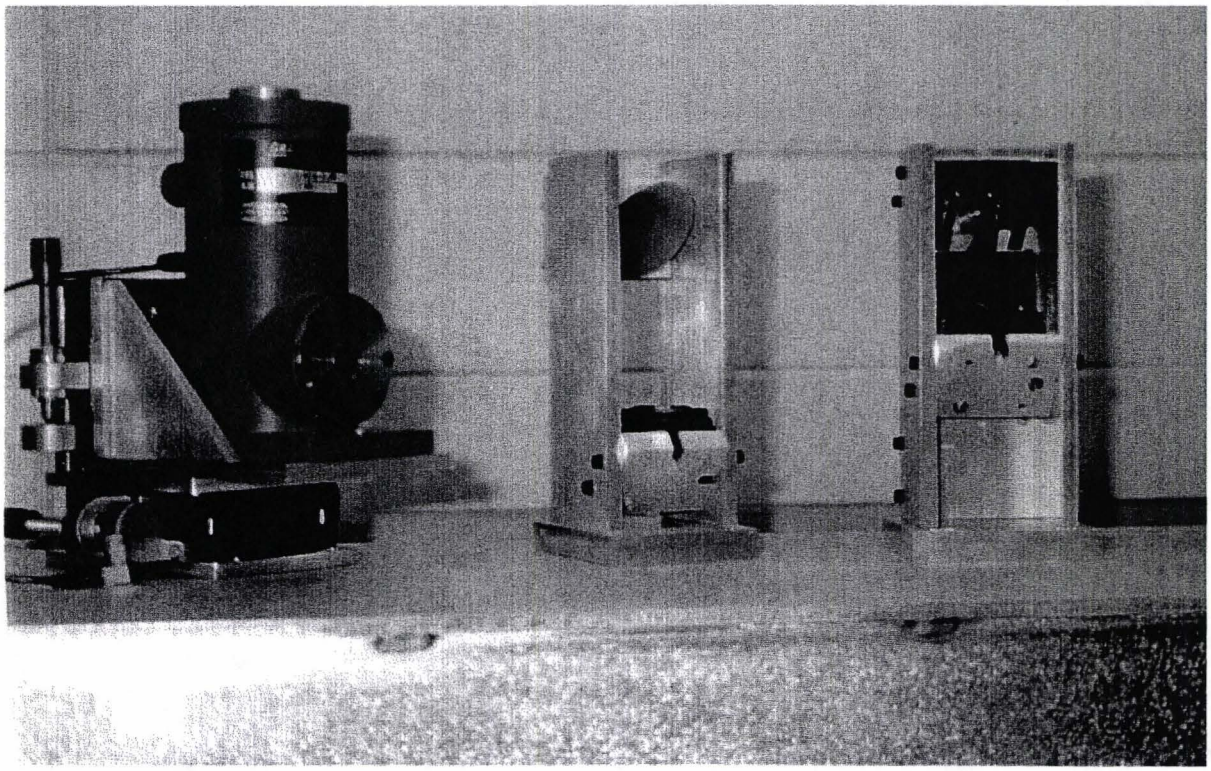

Executive Summary

Rationale for and scope of work. The annual amount of global biomass burning is likely sufficient to have a strong, but, as yet, incompletely characterized, influence on local-global atmospheric chemistry. New optical technology is well-suited for continuous, interference free, measurement of a broad range of reactive and stable gases emitted by fires, including some which are difficult to measure by other methods. We have performed open-path, in-situ, Fourier transform infrared (FTIR) spectroscopic measurements of initial emissions from biomass fires. These measurements have contributed an important body of results relating fire production of greenhouse gases, air toxics, reactive species, and key precursors to chemical and physical properties of the fuels, fuel type, and fire characteristics such as combustion efficiency. This has been especially true for ammonia, heavy hydrocarbons, and oxygenated organic compounds.

In addition, partially as a result of our work, it has become clear that most initial biomass fire emissions (with the exception of CO_2 and CH_4) are too chemically reactive to be well-mixed in the troposphere. The atmospheric processing of these initial emissions, occurring in biomass burning plumes and "haze layers," is not well understood and is likely to be significantly different from the more thoroughly studied chemistry of the "clean" troposphere or urban "plumes." Since fires are a significant trace gas source, it follows that it is crucial to better characterize this post-emission processing in order to advance mankind's general understanding of global atmospheric trace gas chemistry and climate.

To address the need for high-resolution data on post-emission processing, we have performed preliminary airborne FTIR measurements of a suite of compounds on large isolated biomass burning plumes. These measurements have been performed both near the source, to initialize the data set and to validate our lab work, and downwind (including in regional "haze layers") to investigate the important atmospheric transformations of the initial fire emissions. These measurements have been accompanied by measurement of the relevant meteorological parameters and thus are of particular value for comparison and validation of chemistry/transport (C-T) models. In turn, validated C-T models of the atmospheric processing of biomass fire smoke could allow improved estimates, scaling, and predictions of the atmospheric impacts.

In summary, taken together, this information will advance our understanding of the impacts of biomass burning on atmospheric trace gas chemistry and climate at local to global scales. It will also aid in the development of validated "smoke C-T" models and, ultimately, effective mitigation strategies.

Organization of this report. The results in this report are organized as follows. An introductory section lists each stated objective of RJVA 95009, regrouped by topic, followed by a brief discussion of the progress to date in that area. In most cases, the discussion also refers the reader to the publication resulting from this work which contains more details. A copy of each of these nine detailed publications is then attached.

1. Objectives of RJVA95009 and the progress towards these goals.

1.1 Complete the pioneering application of FTIR to emissions characterization.

A. Using the data generated by the Fourier Transform Infrared Spectrometer (FTIR) from the National Center for Atmospheric Research (NCAR) as operated by Dr. David Griffith, complete the development of emission ratios and emission factors for a wide range of fuel types.

B. Model the emission factors as a function of combustion efficiency by fuel type and evaluate the difference in ratios between fuel types.

New methods of spectral data analysis were developed, validated, and then applied to the NCAR spectra. Details were published in the attached publication **R. J. Yokelson, D. W. T. Griffith, J. B. Burkholder, and D. E. Ward, Accuracy and Advantages of Synthetic Calibration of Smoke Spectra, in *Optical Remote Sensing for Environmental and Process Monitoring*, pp. 365-376, Air & Waste Manage. Assoc., Pittsburgh, PA., (1996).**

The simultaneous measurements made of fuel mass loss, stack gas temperature, and total mass flow up the stack were integrated with the FTIR results. This resulted in combustion-process-specific and fire-integrated emission factors for the 16 most common gases emitted by fires. It was possible to classify the products detected by the type of process that dominates in producing them. Carbon dioxide was the dominant emission of (and primarily produced by) flaming combustion, from which we also measured nitric oxide, nitrogen dioxide, sulfur dioxide, and most of the water vapor from combustion and fuel moisture. Carbon monoxide was the dominant emission formed primarily by smoldering combustion from which we also measured carbon dioxide, methane, ammonia, and ethane. A significant fraction of the total emissions was unoxidized pyrolysis products; examples are methanol, formaldehyde, acetic and formic acid, ethene (ethylene), ethyne (acetylene), and hydrogen cyanide. Relatively few previous data existed for many of these compounds and they are likely to have an important, but as yet poorly understood, role in plume chemistry. The fuels were pure pine needles or sagebrush or mixed fuels simulating forest-floor, ground fires; crown fires; broadcast burns; and slash pile burns. Large differences in emissions occurred from different fire and fuel types, and the observed temporal behavior of the emissions was found to depend strongly on the fuel bed and product type. Details were published in the attached publication **R. J. Yokelson, D. W. T. Griffith, and D. E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, *J. Geophys. Res.* 101, 21067 (1996).**

1.2 Develop state-of-the-art, FTIR-based Laboratory measurement program.

C. Using the new FTIR, verify the *relations* for two fuel types developed for objectives A and B above.

F. Two main fuel types will be used to verify the *performance* of the new FTIR (ponderosa pine needles and sagebrush).

The new FTIR has been used in four major laboratory experiments which have verified excellent performance. Emission factors and CE results from 30 fires were successfully measured and published for carbon dioxide, carbon monoxide, methane, ethane, ethene, ethyne, propene, formaldehyde, 2-hydroxyethanal, methanol, phenol, acetic acid, formic acid, nitric oxide, ammonia, hydrogen cyanide, and carbonyl sulfide. The new FTIR gave us the first optical, *in-situ* smoke measurements of phenol and carbonyl sulfide, and the first ever report of 2-hydroxyethanal as a product of fires. The higher time resolution of the new system allowed unprecedented success in assigning the combustion products to specific combustion phenomena and observed smoke appearance. About one-half of the detected organic emissions arose from fuel pyrolysis which produces white smoke rich in oxygenated organic compounds. Most of the observed alkane and ammonia production accompanied glowing combustion without visible smoke, as detailed primarily in the attached publication **R. J. Yokelson, D. E. Ward, R. A. Susott, J. Reardon, and D. W. T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, *J. Geophys. Res.* 102, 18865 (1997)**. These results also include the first optical, *in-situ* measurements of smoke composition from fires in grasses; hardwoods; duff; and litter; and the first ever published, detailed emissions characterization for burning organic soils. NH_3 is normally the major nitrogen-containing emission detected from smoldering combustion of biomass, but from some smoldering organic soils HCN was dominant. Laboratory emission factors and combustion efficiency (CE) were published for ponderosa pine needles (PPN), PPN and wind, PPN and wind and fire retardant, sagebrush, Douglas Fir, and poplar shavings in the attached publication **R. J. Yokelson, D. W. T. Griffith, R. A. Susott, and D. E. Ward, Spectroscopic Studies of Biomass Fire Emissions, in *International Perspectives on Landscape Fires,* edited by J. Greenlee, in press, International Assoc. of Wildland Fire, Fairfield, WA., (1997)**. The new FTIR was also successfully deployed on a unique 3-FTIR experiment with collaborators from NASA. Our FTIR successfully measured CE and EF's while the other two FTIR's simultaneously measured the radiative emissions. These results are currently in preparation.

1.3 Develop state-of-the-art, FTIR-based field program.

E. Determine and carry out the best method to integrate the data acquisition from the new FTIR system with the existing IFSL instrumentation. This will be important to streamline FTIR data reduction and to verify FTIR performance.

H. To determine/devise the most promising methods for incorporating the FTIR into the IFSL field measurement program (including airborne applications) and to provide a rigorous, preliminary assessment of these methods.

J. During the summer of 1997 in Alaska, collect data using the FTIR on board the Forest Service air quality monitoring aircraft. This involves determining the similarity of smoke collected over full-scale field fires in comparison to results from laboratory fires.

A new type of airborne smoke-sampling system consisting of a Fourier transform infrared spectrometer coupled to a "flow-through" multipass cell was designed and deployed for the first time. Measurements were conducted in North Carolina and Alaska on large, isolated plumes both near the source and downwind. Spectra acquired within a few kilometers of the fires yielded excess smoke concentrations for at least 9 species including: H_2O, CO_2, CO, CH_4, H_2CO, CH_3COOH, CH_3OH, C_2H_4, and NH_3. This was easily the most successful ever deployment of an FTIR and White cell in an aircraft and it provided unambiguous field verification of the high concentrations of oxygenated organic compounds previously observed in our laboratory fires. The system design details, a preliminary performance assessment, and initial results were presented at an international meeting: **R. J. Yokelson, J. G. Goode, R. A. Susott, R. E. Babbitt, D. E. Ward, S. P Baker, W. M. Hao, and D. W. T. Griffith. Smoke chemistry measurements by airborne Fourier transform infrared spectroscopy (AFTIR). presented at IGAC International Symposium on Atmospheric Chemistry and Future Global Environment, 11-13 November, 1997, Nagoya, Japan**. Publication of the final results in JGR is anticipated later this year. Important simultaneous measurements were made with existing IFSL instrumentation including temperature; pressure; GPS; airborne sonde; real-time particulate, CO, and CO_2; and integrated filter and canister samples. Currently this data can be rigorously overlapped because the data logger for the other IFSL instruments records the time when the FTIR inlet/outlet valves are opened and closed and this cycle has a marked appearance in the FTIR data. Logging auxiliary data on the FTIR computer is possible, but so far only at reduced sampling rates. so this option was not used for the airborne experiment.

1.4 Provide scientific support for the risk assessment carried out by the National Wildfire Coordinating Group regarding wildland firefighter exposure to smoke.

G. Identify and quantify a few of the important air toxin and irritant species found in smoke that are detectable and provide sufficient resolution for quantification using the new FTIR system.

Any of the 89 *gases* defined as hazardous air pollutants (HAPS) by the EPA would be detectable in smoke by FTIR if they were present at high enough levels to be a health concern. The following HAPS were detected in smoke by FTIR and thus evaluation of exposure levels was warranted: carbon monoxide, methane, ethane, ethene, ethyne, propene, formaldehyde, 2-hydroxyethanal, methanol, phenol, acetic acid, formic acid, nitric oxide, ammonia, hydrogen cyanide, sulfur dioxide, and carbonyl sulfide. Undetected HAPS must have been present at levels far below the exposure limit in the fires we studied. Of the HAPS detected, only carbon monoxide and formaldehyde were present at levels that approached exposure limits. The basic results are clearly presented in the papers previously cited. Also, two articles (attached) were written for the **Health Hazards of Smoke** (HHS) newsletter to explain our contribution to the risk assessment in terms appropriate for the firefighting community. Topics covered in these articles were, estimating firefighter exposure from smoke composition data, comparison of estimated exposures to the "safe" limits, how FTIR works, and the use of technique intercomparison to determine the accuracy of estimated exposures. Our findings were also presented as a talk and poster, and as participation in a panel discussion at the national HHS synthesis conference in April 1997. In addition, our technique was filmed for a HHS video.

Our FTIR measurements contributed strongly to the risk assessment because we directly measured peak levels in rapidly changing smoke mixtures and because the FTIR technique is essentially interference free. Inexpensive sensors for acrolien deployed in a field study suggested that exposure to this compound was of concern. In fact, exposure to this compound is "driving" the current risk assessment. However, this compound is not evident in the FTIR smoke spectra checked to date. This suggests two valuable follow-up studies: 1. deployment of the FTIR in a fireline situation, and 2. intercomparison of the FTIR and the "acrolien badge" under controlled laboratory conditions.

1.5 Develop capability to model atmospheric chemistry and transport in biomass burning plumes.

I. To work with Dr. Richard Field of the University of Montana (current Principal Investigator of a Research Joint Venture Agreement No. INT-95084-RJVA, entitled "Atmospheric Processes in Plumes of Biomass Fires") in establishing realistic initial conditions and emissions processing scenarios for use with the National Center for Atmospheric Research "Master Atmospheric Chemical Model."

My association with Field started with a series of extensive discussions on atmospheric chemistry which constituted an informal "short course" on this topic. I also recommended a large number of papers I had read on smoke modeling and located three different atmospheric modeling programs to assist Field in developing his own modeling strategies. These concepts were strengthened by co-authoring two proposals to support modeling activities. Field and his graduate student attend our weekly meetings to discuss the literature of atmospheric chemistry. I have provided them (on at least three occasions) with realistic initial conditions and dilution rates for smoke plumes. In addition, I have suggested a series of modeling experiments which would help determine the relative contribution of several different precursors to ozone production. Some preliminary model predictions are just becoming available.

Most of the previously cited papers specifically address atmospheric modeling and in addition one paper was also produced to assist in the compilation of national trace gas emissions inventories: **R. J. Yokelson, R. A. Susott, R. E. Babbitt, D. E. Ward, and W. M. Hao. Trace gas emissions from specific biomass fire-types. in (Proceedings)** ***START Synthesis Workshop on Greenhouse Gas Emission, Aerosols and Land Use and Cover Change in Southeast Asia,*** **15-18 November 1997, Taipei in press.**

1.6 Measure the accuracy of IFSL laboratory apparatus for carbon mass-balance determinations.

D. Validate the use of the IFSL Combustion Laboratory for making carbon mass flux determinations and demonstrate the comparability to mass loss rates for the combined water and carbon loss from the fuel beds.

For one month during the summer of 1995 I carried out intensive testing of the combustion laboratory and related infrastructure. The basic purpose was to determine the accuracy of the mass-balance approach and to test a related theory for treating fuel moisture evolution in the mass balance. In this theory it is assumed that, for fine fuels, to a good approximation, the fuel moisture is vaporized during initial flaming combustion which results in CO_2 and H_2O. The ratio H_2O/CO_2 from complete combustion is determined by the C:H ratio of the fuel and this water is known as the combustion water (CW). Then the fuel moisture (FM) vaporized is given by equation (1)

$$(1) \quad FM = TW - BW - CW$$

where TW and BW are total and background water respectively. Fuels used for these tests were ethanol (0% FM), excelsior, and bluegrass. The methods included:

1. CO_2 and water by Licor 6262 which was very precisely calibrated with intensive consultation with the manufacturer.
2. CO_2 and CO from the FASS packages.
3. Flow and flow profile by Kurz model 560 "hot wire" flow meter and by the FASS anemometers which were thoroughly intercompared with each other and the Kurz.
4. Temperature by thermocouple calibrated at ice and boiling of water to within 0.1 °C.
5. Mass loss by digital balance (calibration checked by standard weight).
6. Fuel moisture by digital scale and oven drying.
7. Measurement of the thermal boundary layer (expected to be wider than the flow boundary layer in a stack) by a TC array.

The results of the tests were very satisfactory and have been kept neatly organized in a notebook, but not published.

Selected Publications Resulting From RJVA95009

R. J. Yokelson, D. W. T. Griffith, J. B. Burkholder, and D. E. Ward, Accuracy and Advantages of Synthetic Calibration of Smoke Spectra, in *Optical Remote Sensing for Environmental and Process Monitoring*, pp. 365-376, Air & Waste Manage. Assoc., Pittsburgh, PA., (1996).

R. J. Yokelson, D. W. T. Griffith, and D. E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, *J. Geophys. Res.* 101, 21067 (1996).

R. J. Yokelson, D. E. Ward, R. A. Susott, J. Reardon, and D. W. T. Griffith, Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy, *J. Geophys. Res.* 102, 18865 (1997).

R. J. Yokelson, D. W. T. Griffith, R. A. Susott, and D. E. Ward, Spectroscopic Studies of Biomass Fire Emissions, in *International Perspectives on Landscape Fires,* edited by J. Greenlee, in press, International Assoc. of Wildland Fire, Fairfield, WA., (1997).

D. E. Ward and R. J. Yokelson, Progress in Smoke Characterization and Modeling, in *Transboundary Pollution and the Sustainability of Tropical Forests: Towards Wise Forest Fire Management*, in press, ASEAN Institute of Forest Management, Kuala Lumpur, (1997).

R. J. Yokelson, J. G. Goode, R. A. Susott, R. E. Babbitt, D. E. Ward, S. P Baker, W. M. Hao, and D. W. T. Griffith. Smoke chemistry measurements by airborne Fourier transform infrared spectroscopy (AFTIR). presented at IGAC International Symposium on Atmospheric Chemistry and Future Global Environment, 11-13 November, 1997, Nagoya, Japan.

R. J. Yokelson, Health Hazards of Smoke, Fall 1995, "Firefighter Exposure to Air Toxics."

R. J. Yokelson, Health Hazards of Smoke, Spring 1996, "Smoke Studies."

R. J. Yokelson, R. A. Susott, R. E. Babbitt, D. E. Ward, and W. M. Hao. Trace gas emissions from specific biomass fire-types. in (Proceedings) *START Synthesis Workshop on Greenhouse Gas Emission, Aerosols and Land Use and Cover Change in Southeast Asia,* 15-18 November 1997, Taipei in press.

Accuracy and Advantages of Synthetic Calibration of Smoke Spectra

R. J. Yokelson
D. W. T. Griffith
J. B. Burkholder
D. E. Ward

in

Optical Remote Sensing for Environmental and Process Monitoring

Proceedings of the Air and Waste Management Association Symposium

San Francisco, Sept. 25-27, 1995

Accuracy and Advantages of Synthetic Calibration of Smoke Spectra

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ABSTRACT

Open-path FTIR (OP-FTIR) when combined with synthetic calibration allows some inherent advantages of optical remote sensing (ORS) techniques to be realized, with good accuracy, in the study of smoke from biomass fires while eliminating the time-consuming requirement for laboratory acquisition of a large number of elevated temperature reference spectra.

INTRODUCTION

Biomass is an abundant renewable fuel[1] and biomass burning is a key to the most energy-efficient system of food production in the tropics.[2] However, biomass burning also injects significant amounts of trace gases to the atmosphere on a global scale and often causes significant air pollution on a regional scale.[3] For these reasons it is desirable to study biomass burning emissions with an OP-FTIR technique. Some of the advantages are:

- Simultaneous measurements of a wide variety of species, including reactive gases, with good selectivity.
- Continuous, real time measurements allow dynamic processes to be followed and may reduce some o the uncertainty associated with grab sampling.
- Location and identification of unanticipated species by screening spectra.

For the above advantages to be realized the analysis of congested smoke spectra acquired at many different temperatures must be efficient. In this respect, synthetic calibration CLS[4] offers much promise as it eliminates the need (in this application) to acquire reference spectra for a large number of compounds at many temperatures. The synthetic calibration CLS procedure is also readily automated. We describe a "proof of principle" experiment which demonstrates both a successful application of synthetic calibration to the analysis of smoke spectra and that the inherent advantages of an OP- FTIR technique are realized, adding substantially to our understanding of the combustion chemistry of biomas.

EXPERIMENTAL

The smoke spectra were collected in 1989 and the experimental configuration has been described in detail elsewhere.[5,6] Biomass fuels were burned on a 1 x 2 m continuously-weighed bed, and the smoke was captured by a 3.6 meter inverted funnel above the fuel bed and directed through a 1.5 meter diameter stack. 15 meters above the fuel bed, the collimated IR source was transmitted twice across the stack for a total smoke absorption path of 3 m, then focused and re-collimated into an EOCOM interferometer with a Ge/KBr beamsplitter and InSb/MCT sandwich detector. Spectra were alternately recorded by the InSb (1800-3900 cm^{-1}) and MCT (700-1900 cm^{-1}) detectors throughout each fire. Resolution was 0.12 cm^{-1} and 5-20 scans were typically coadded over 0.5 to 2 minutes for each spectrum. The higher time resolution (and less signal averaging) was used near the beginning of the fire when temperature changes rapidly. The spectra recorded before the fire were used to determine background levels of H_2O, CO_2, CO and CH_4, and to serve as background spectra to create absorbance spectra from spectra collected during the fire when required.

Simultaneous (independent) measurements included flow by a mass flow meter (Kurz, Model 455), temperature by thermocouple gauge, CO and CO_2 by NDIR (Horiba PIR-2000), and NO and NO_X by chemiluminesence (Thermoelectron Model 42). Samples for the simultaneous gas measurements were drawn from the center of the stack near the FTIR beam through approximately 30 m of .25" o.d. teflon tubing. These measurements were logged every 5 s. The fuel bed mass was also recorded every 30 s for some fires. Atmospheric pressure at the site was 90.9 ± 0.4 kPa and temperature in the stack gas absorption path ranged from 300 to 420 K.

Data Reduction

Three different procedures were followed to determine trace gas concentrations from spectra. For most gases, classical least-squares (CLS) fitting of *calculated* calibration spectra to the measured spectra in selected spectral regions was the method of choice. For species where this was not applicable, either interactive spectral subtraction or peak-height-based analyses using reference spectra were used.

Synthetic Calibration CLS. The computer program MALT[4] (Multiple Atmospheric Layer Transmission) computes ideal spectra from HITRAN absorption line parameters;[7] convolves these spectra with the instrument function such that the calculated spectra closely match real experimental spectra; and generates a set of calibration spectra over a range of gas concentrations for conventional quantitative analysis using classical least-squares (CLS) methods.[8] The MALT/CLS method is described in detail elsewhere.[4] The smoke spectra were surveyed to identify the absorbers and with careful consideration of interferences and dynamic range a set of optimum small spectral regions was selected for each gas or gases of interest. For each region, a set of calibration spectra was calculated at 10 K intervals from 290 to 420 K and the analyses of measured spectra were carried out using calibration spectra calculated at the temperature nearest the measured temperature at the time the spectrum was recorded. Figure 1 shows an example of a MALT/CLS fit to a experimental smoke spectra, for CO/CO_2 at 2211-2243 cm^{-1}.

Time requirements for synthetic calibration CLS procedure. The LABCALC/GRAMS, K-matrix CLS "concentration retrieval" routine was rewritten so that it only requires a spectral window and the name of a file which lists each spectra and its acquisition temperature as inputs for a specific fire. The adapted routine then performs the CLS analysis for that window for all the spectra in the fire in a few seconds. In order for this adapted CLS routine to run it must have access to a library of calibration matrices at each temperature. MALT calculates a typical set of calibration spectra consisting of 20 mixtures of 5 components at 14 temperatures in under 2 minutes with a 60MHz processor. The set of calibration spectra is converted to a set of calibration matrices by modified K-matrix software. This set of calibration matrices need only be calculated once per window as the calibration matrices are transferable to any spectra measured with the same instrumental parameters. (Run-time for MALT is slightly increased if a component proportional to the square of concentration is included and can be significantly reduced if approximations are justified about the linewidths.) MALT/CLS can also be used

with species not included in HITRAN. For example, for HCOOH, the spectral line parameters were blended into the HITRAN database using the HAWKS (Ontar Corp.) software. The retrieval steps can be incorporated into an instrument driver which can then monitor air unattended.[4] In summary, once the windows have been optimized and the libraries set up the analysis is essentially instantaneous.

Conventional Retrievals. For CH_3OH, C_2H_4, CH_3COOH and terpenes spectral line parameters were not available and traditional methods are used. For CH_3OH, a prominent Q-branch feature appears near 1033 cm^{-1}, overlapped by single lines of NH_3. Each spectrum measured during the fire was ratioed to the spectrum collected before the fire to form an absorbance spectrum. A MALT-calculated NH_3 spectrum at the correct temperature was then interactively subtracted from the measured spectrum, followed by subtraction of a laboratory reference spectrum of 36.1 ppmv CH_3OH in 1 atm N_2 recorded on a Bomem DA3 FTIR spectrometer at 0.12 cm^{-1} resolution. The CH_3OH spectrum was assumed to be temperature independent over the ≡ 30 K range that CH_3OH was observed. For C_2H_4, CH_3COOH, and terpenes the concentrations were based on peak heights from reference spectra we measured or that are published at the appropriate resolution.[9]

RESULTS AND DISCUSSION

Simultaneous concentration time series could be determined for most of each fire for fourteen species; carbon dioxide, carbon monoxide, methane, ethane, ethene, ethyne, formaldehyde, methanol, acetic acid, volatile higher hydrocarbons (terpenes), water, nitric oxide, nitrogen dioxide, ammonia and sulfur dioxide. Three other species were measurable only during periods of peak emissions for some fires; formic acid, hydrogen cyanide and carbonyl sulfide.

Quality Control Aspects For This Experiment

Using the synthetic calibration method with good quality spectra[4] (signal:noise ratio (S:N) > 1000) allows precision (normally) better than 1% and absolute accuracy better than 2%. However, in these spectra, the S:N is typically around 100. This is primarily due to thermal variation in the sample, the short pathlength and measurement time and the optical configuration which did not modulate the light before probing the sample. The S:N in the spectra determines detection limits and a lower limit to precision. This is ≡ 1 ppm for most species analyzed by MALT/CLS, and for spectral subtraction or peak-height analyses.

Precision. The precision of our measurements can be estimated from the variation in concentrations retrieved from the same spectra, but from different spectral regions. We investigated this most extensively for CO since it was the most challenging molecule to analyze due to a high dependence on assumed temperature, narrow linewidths, and large dynamic range. Spectral windows were developed in three locations for CO: the high energy end of the R-branch (see Figure 1); the low energy end of the P-branch; and the strongest peak of the ^{13}CO R-branch. These windows were all used to retrieve concentrations from the fire that exhibited the highest levels of CO. Figure 2a shows these results plotted along with the average of the 3 windows. In Figure 2b the value from the R branch window minus the average of all three windows is shown as one possible estimate of precision. The precision appears quite good as the arbitrarily selected window returns values that are 1.25 ± 1.61% (1σ) lower than the average value.

Simultaneous analyses from two or more independent spectral regions was also possible for CH_4, NH_3, and NO and for these species agreement was normally within 5% (1σ) at concentrations well above the detection limit. The reported value for these species is the average value of the replicate determinations.

Accuracy. Accuracy can be estimated as follows. The precision (limited by the accuracy of the HITRAN parameters and the experimental S:N) can be taken as 5% based on the results described above. In addition, we find the MALT/CLS analysis has a species dependent sensitivity as high as 1% K^{-1} to assumed temperature. We estimate that rounding of the analysis temperature to the nearest 10 K, and the variation in temperature, while coadding scans or across the stack (both effects are significant only

during the first moments after ignition), introduces an additional error of 5%. In summary, we estimate total error in single gas concentration measurements of 7% (1σ) or 1 ppmv, whichever is higher.

Our estimate of error can be compared with the variation between the FTIR measurement and simultaneous measurements by extractive point sampling. Figure 3a shows the comparison of the CO R-branch window with the NDIR data in real time. There is good relative agreement between the two CO measurements. In Figure 3b the FTIR and NDIR values from the same fire are plotted against each other to estimate any bias between them. In this case the FTIR concentrations are about 7% higher. Figure 3c shows the real-time comparison of FTIR and NDIR measurements of CO_2 for the fire with the highest CO_2 concentrations. The comparison again shows excellent relative agreement but with FTIR measurements systematically ca. 7% higher than NDIR. Similar comparison of NO by FTIR and chemiluminescence show agreement within 10%. Part of the discrepancies between the FTIR and simultaneous independent measurements may be due to sample line losses or nonlinear effects with the conventional analyzers or to the difference in gas probed by the open-path and point sampling techniques.[10] An error estimate for the conventional analyzers was not completed. In summary, the level of agreement suggests that our initial error estimate is reasonable.

There were no canister samples taken during these fires, but we can compare our results with literature results based on canister sampling of similar field fires. In Figure 4a we plot our methane emission factors against modified combustion efficiency[5] along with results based on canister sampling from aircraft[11, 12] and towers[13] (in all cases for mixed coniferous fuels). The slopes from the three measurement types are in excellent agreement given the limitations of the various methods

In Figure 4b we compare our methanol results with results from laboratory fires, in similar fuels, analyzed by a "cryotrapping" - GC/MS method[14]. The FTIR data are highly correlated and show much higher emission factors than the other study. The comparison for acetic acid gives similar results.[5] Direct comparisons are needed to elucidate the reasons for these differences.

Advantages of OP-FTIR Measurements.

A number of the anticipated advantages of the open-path FTIR technique were realized and increased our understanding of biomass fires. These developments have been described elsewhere[5] and are only summarized here.

Real Time. Figure 5 shows that there are at least three major processes which contribute to the emissions from a single fire and that the dominant contributions of these processes may come at different times. This has obvious implications for grab-sampling programs.

Reactive Gases. Figure 6 shows that reactive gases typically account for over one-half of the fuel nitrogen and more than a third of the organic emissions. Thus the ability to measure these gases is significant.

Finding unknowns. Light NMHC's have been the focus of many biomass burning studies and a number of models of plume chemistry have been developed including these compounds. In contrast there have been no published measurements of terpenes in smoke nor have these reactive compounds been included in plume chemistry models. Figure 7 shows the C-H stretch region of a smoke spectrum. The spectra of some light NMHCs and typical terpenes are also included. The smoke spectrum more closely resembles the terpenes than the light NMHC's and this suggests that these compounds should be included in future models of biomass smoke chemistry.

CONCLUSIONS

Synthetic calibration resulted in significantly reduced time requirements for analysis of smoke spectra while providing good accuracy. The reduced analysis time enhanced the realization of the inherent advantages of OP-FTIR which showed that biomass-fire smoke varies in composition in a complex manner and contains significant amounts of reactive gases, probably including terpenes.

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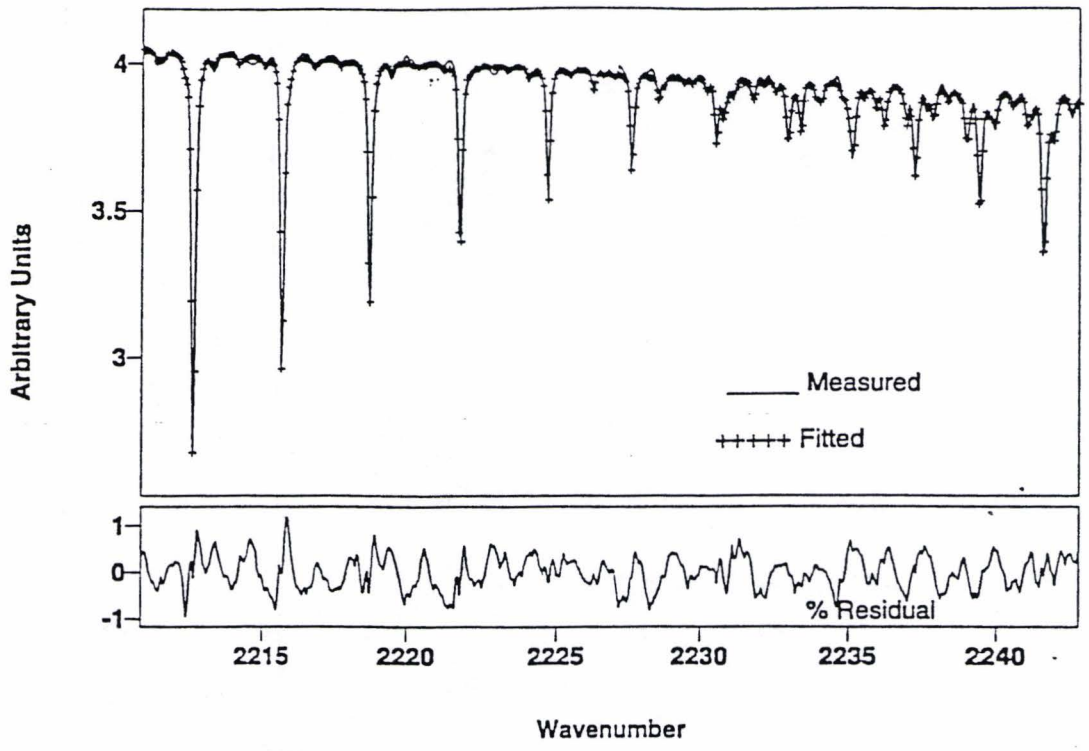


Figure 1. MALT/CLS measured, fitted, and % residual (=(fitted-measured)*100) spectra for a typical window. Lines from 2210 to 2235 cm^{-1} are due to CO and lines from 2232 to 2245 cm^{-1} are due to CO_2. Mixing ratios determined from the spectra are 210 ppm CO and 1717 ppm CO_2. H_2O and N_2O are included in the fit.

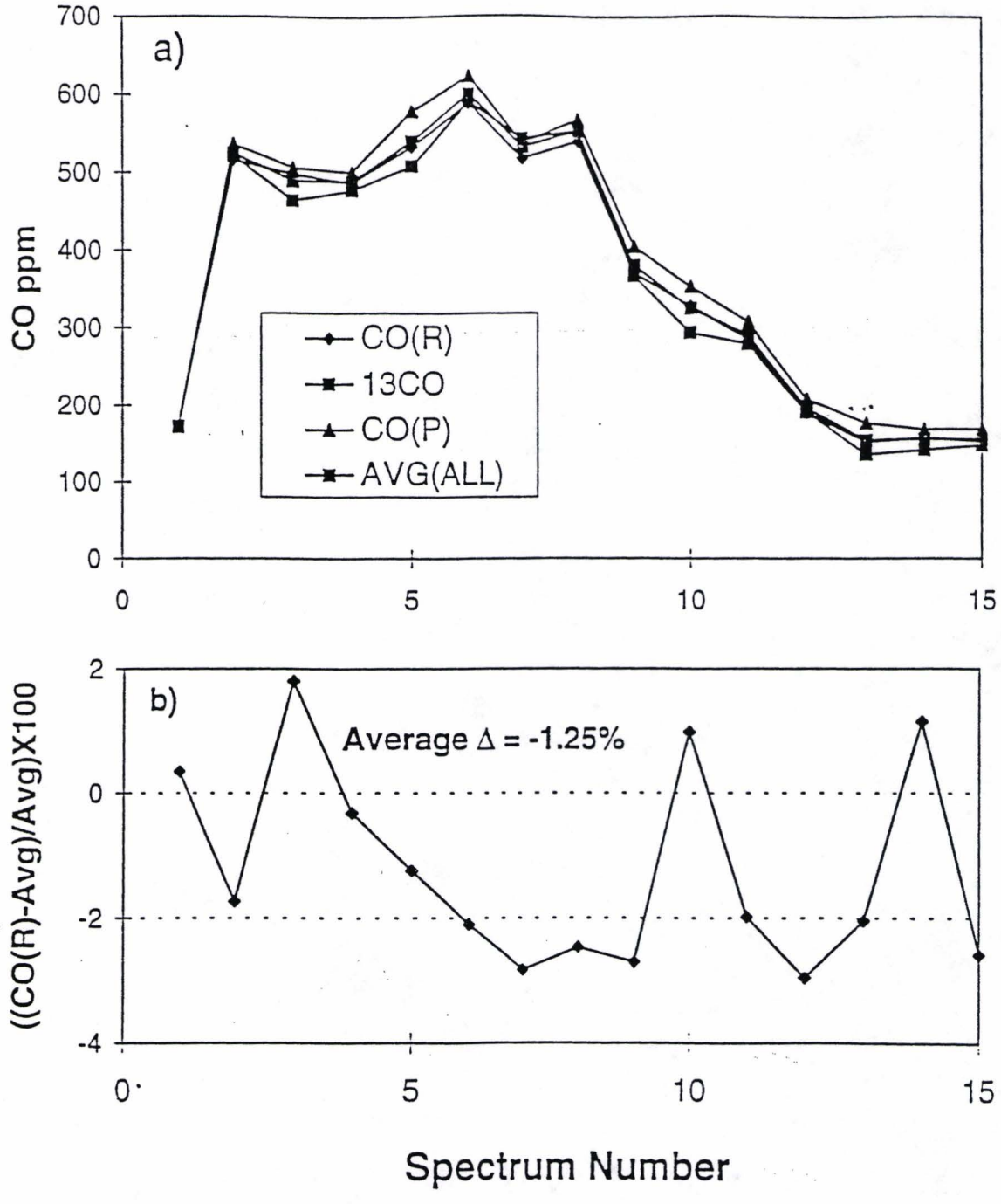


Figure 2. The concentrations and precision for CO derived from 3 spectral regions are shown.

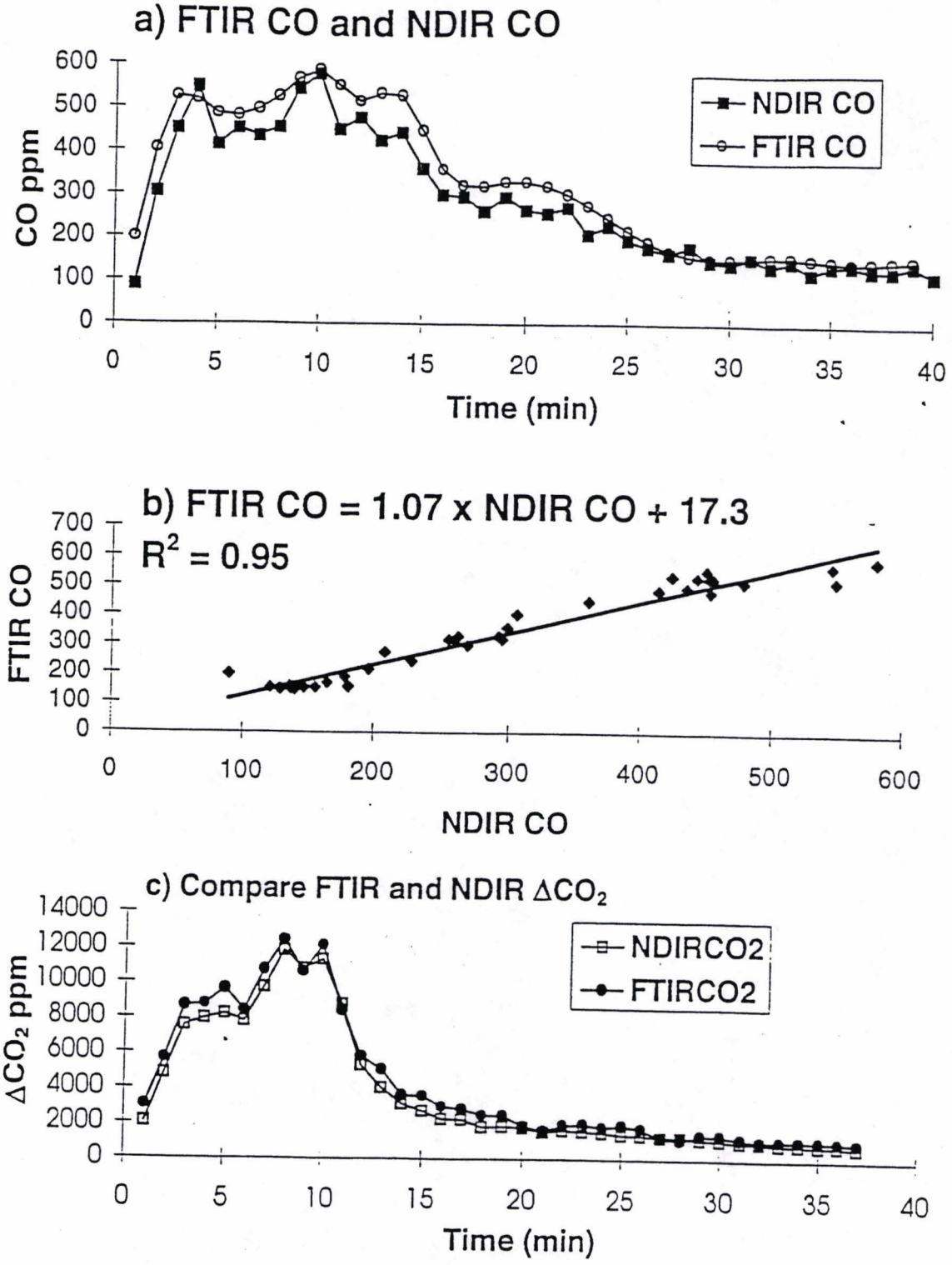


Figure 3. Intercomparison of FTIR and NDIR data.

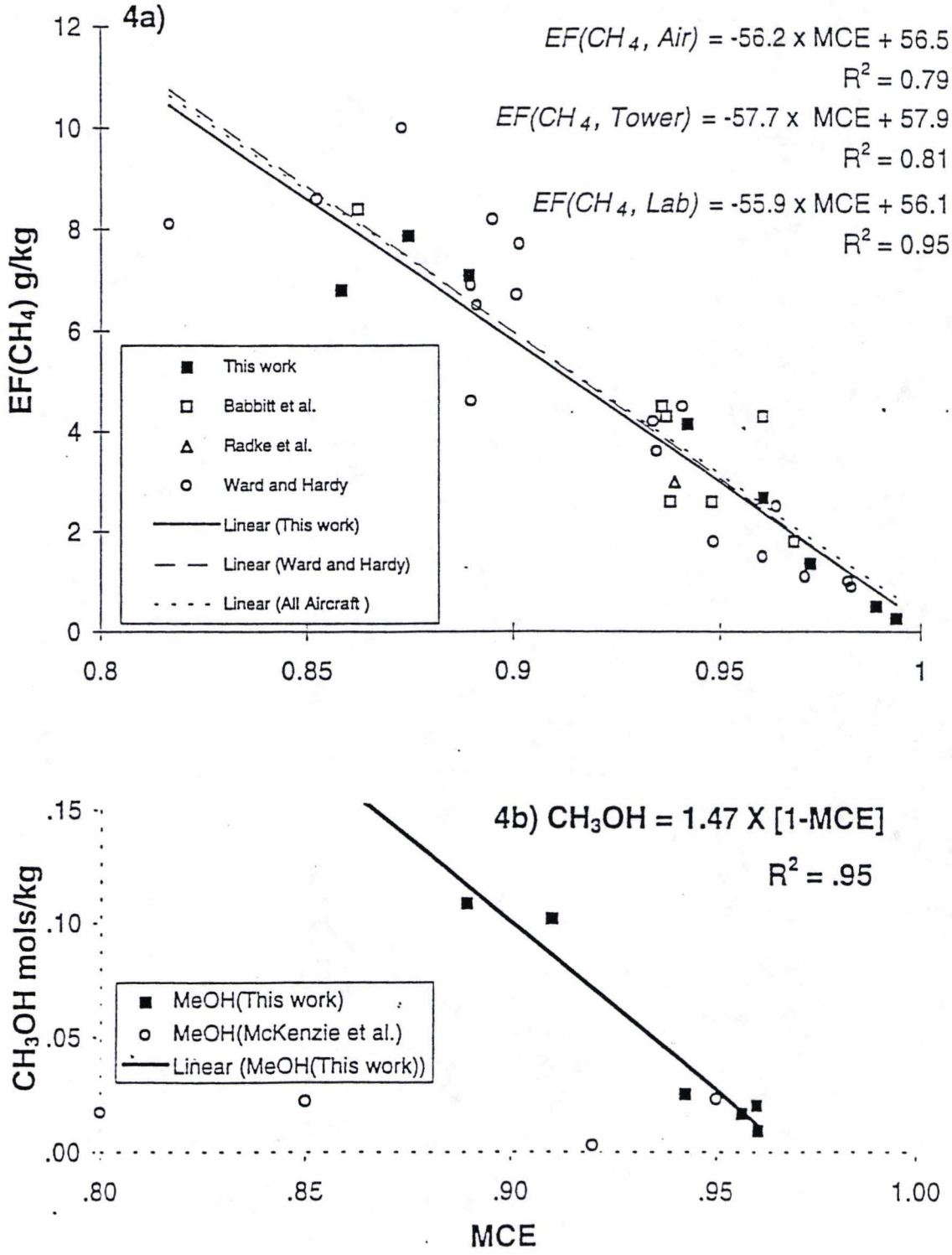


Figure 4. Intercomparison of FTIR data with literature data in similar fuels.

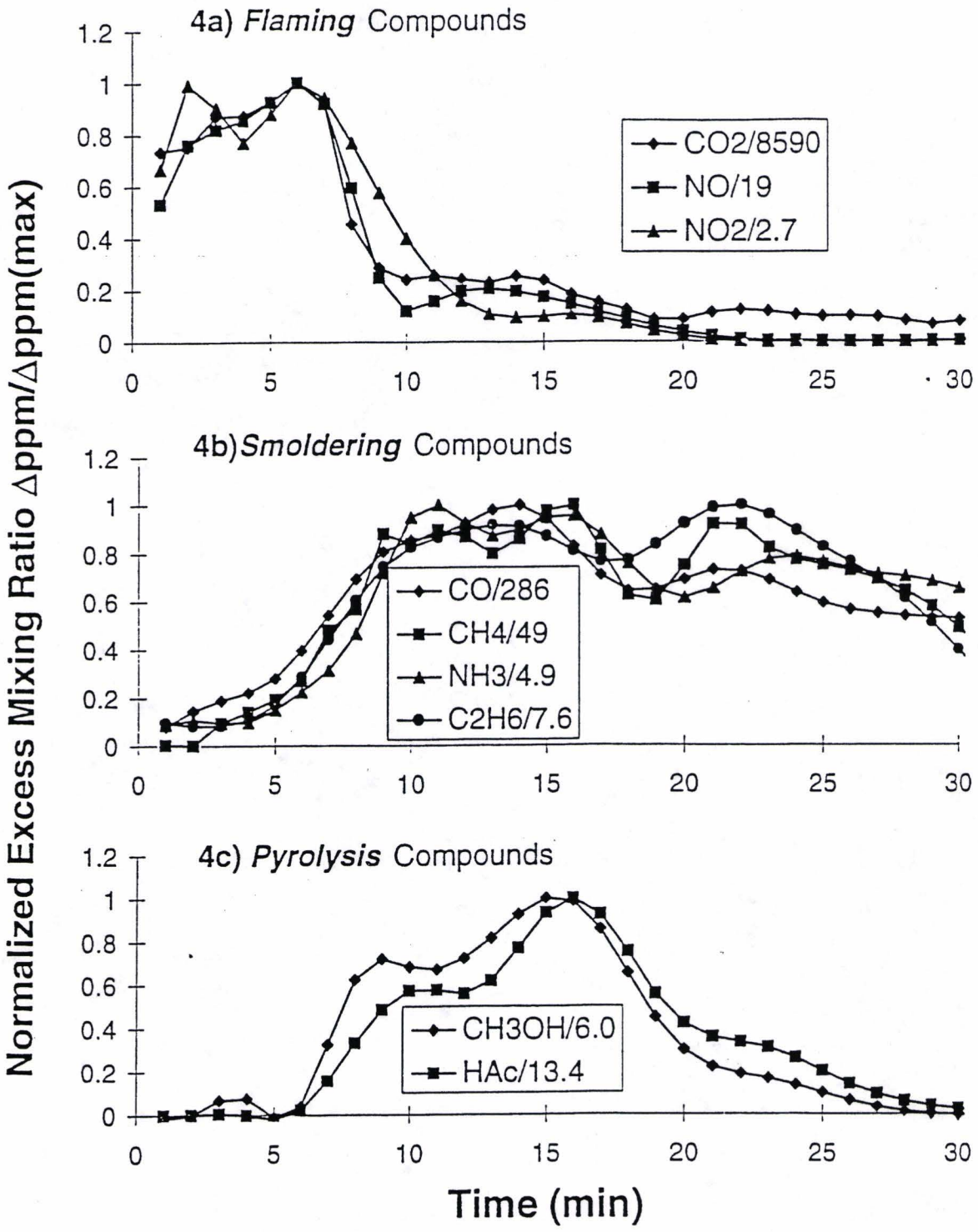
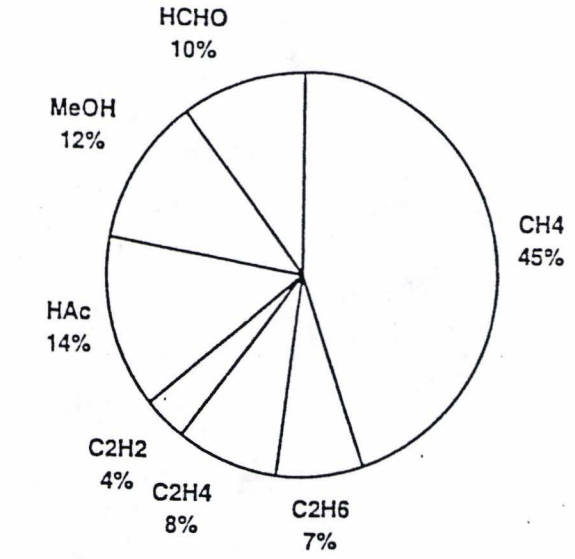


Figure 5. Examples of concentration Vs. time for compounds emitted by different processes occurring during a single fire.



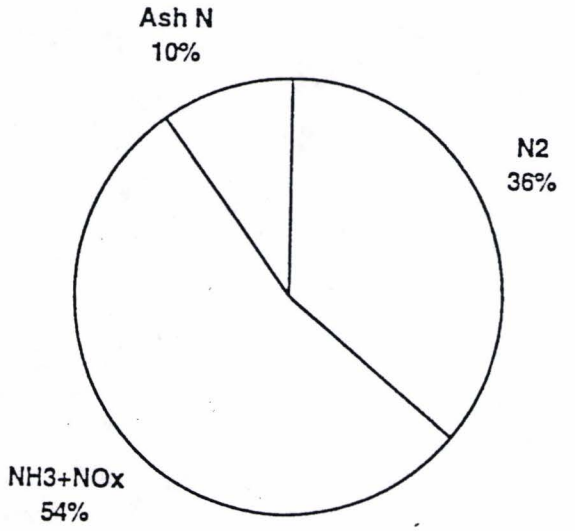


Figure 6. The top piechart shows a breakdown for detected organic emissions from a single fire. The lower piechart shows the fate of the fuel N; deduced as described in Reference 5. In both cases a large proportion of the detected gases are reactive and difficult to sample by traditional methods.

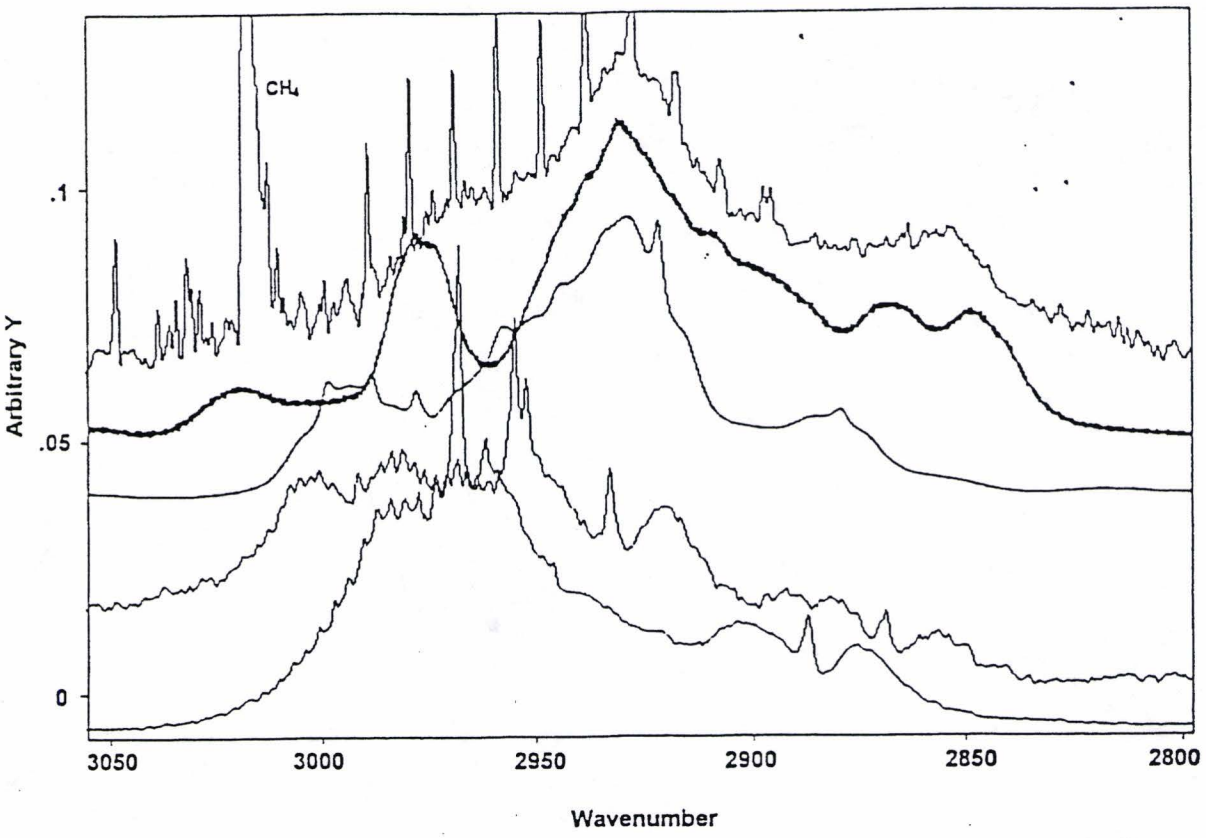


Figure 7. The absorbance spectra from top to bottom are: smoke (including the sharp lines primarily due to H_2O and CH_4), limonene, β-pinene, propene, and propane. The similarity between the smoke and terpene spectra is evident.

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 101, NO. D15, PAGES 21,067–21,080, SEPTEMBER 20, 1996

Open-path Fourier transform infrared studies of large-scale laboratory biomass fires

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Abstract. A series of nine large-scale, open fires was conducted in the Intermountain Fire Sciences Laboratory (IFSL) controlled-environment combustion facility. The fuels were pure pine needles or sagebrush or mixed fuels simulating forest-floor, ground fires; crown fires; broadcast burns; and slash pile burns. Mid-infrared spectra of the smoke were recorded throughout each fire by open path Fourier transform infrared (FTIR) spectroscopy at 0.12 cm^{-1} resolution over a 3 m cross-stack pathlength and analyzed to provide pseudocontinuous, simultaneous concentrations of up to 16 compounds. Simultaneous measurements were made of fuel mass loss, stack gas temperature, and total mass flow up the stack. The products detected are classified by the type of process that dominates in producing them. Carbon dioxide is the dominant emission of (and primarily produced by) flaming combustion, from which we also measure nitric oxide, nitrogen dioxide, sulfur dioxide, and most of the water vapor from combustion and fuel moisture. Carbon monoxide is the dominant emission formed primarily by smoldering combustion from which we also measure carbon dioxide, methane, ammonia, and ethane. A significant fraction of the total emissions is unoxidized pyrolysis products; examples are methanol, formaldehyde, acetic and formic acid, ethene (ethylene), ethyne (acetylene), and hydrogen cyanide. Relatively few previous data exist for many of these compounds and they are likely to have an important but as yet poorly understood role in plume chemistry. Large differences in emissions occur from different fire and fuel types, and the observed temporal behavior of the emissions is found to depend strongly on the fuel bed and product type.

Introduction

Biomass burning injects significant amounts of trace gases and particles into the regional and global atmosphere [*Crutzen and Andreae*, 1990]. Quantification of representative emissions from fires is difficult, and different configurations of analysis techniques and sampling platforms have been utilized. Aircraft can probe a large area of well-mixed, integrated emissions, investigate secondary chemistry, and provide details on transport [*Andreae et al.*, 1988a, b]. However, airborne sampling is expensive; it is difficult to monitor a single fire continuously from beginning to end; and specific knowledge of the fuels and fire types are difficult to correlate with measurements. Ground-based measurements provide the opportunity for more detail on the fire and fuels [*Delmas et al.*, 1991] but may tend to incorrectly estimate the emissions in the convection column above the fire [*Andreae et al.*, 1988a]. Tower-based measurements have been implemented as a means of more representative ground-based sampling [*Ward et al.*, 1992].

There are a number of advantages in studying biomass fires in the laboratory. They include burning under controlled conditions, where the chemical and physical properties of the fuel and environment may be known in detail, and capture of all the smoke for the entire course of the fire so that emission factors for any measurable airborne species can be determined accurately. The laboratory characterization of the products of biomass burning began with work to assess the contribution of forest fires in the southeastern United States to regional air pollution [*Ryan and McMahon*, 1976] and the emissions due to burning agricultural waste [*Darley et al.*, 1966] or wood for heat [*Dasch*, 1982]. This early work often distinguished between flaming and smoldering combustion, distillation and pyrolysis, and normally featured detection of CO_2, CO, and NO_x. Formic acid and acetic acid were later added to the range of products detected in laboratory fires [*Talbot et al.*, 1988]. The laboratory experimental fires of *Lobert et al.* [1991] were the first to characterize a wide variety of emission products of particular importance to atmospheric chemistry.

In addition to the challenges presented by the need to sample fires representatively, there is the additional challenge of

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Paper number 96JD01800.
0148-0227/96/96JD-01800$09.00

identifying instrumental techniques that can cope with hot, reactive samples where the potential for chemical interference and the dynamic range of concentrations is very high. The companion work to the study described here was the first application of open-path FTIR spectroscopy to the analysis of smoke from biomass burning and focused on prescribed fires in sagebrush and forestry operations in the western United States [*Griffith et al.*, 1991]. This paper demonstrated the advantages of an FTIR-based study of biomass fires: (1) Simultaneous measurements can be made of a wide variety of species with good selectivity (i.e., resistance to interference) over a wide range of concentrations with detection limits in the low parts per billion range. (2) Measurements can be made pseudocontinuously in real time so that dynamic processes can be followed. (3) There is no need to take samples and no possibility of sampling- or storage-related artifacts so that reactive gases can be quantified. (4) The measurement is path integrated, averaging over small-scale local variations. It is thus relatively immune to spatial variation compared with point sampling.

This work extends the open-path FTIR field studies of *Griffith et al.* [1991] to controlled fires in a large-scale combustion laboratory at the Intermountain Fire Sciences Laboratory (IFSL). This paper describes a preliminary study in which measurements of smoke composition for up to 16 chemical species from 9 biomass fires were made in October 1989. The study demonstrates the potential of the open-path FTIR technique for laboratory fires and provides a sufficient body of data to yield significant insights into biomass fire emissions. The technique will be further developed and applied with a dedicated FTIR system recently installed in the IFSL combustion laboratory.

Methods

Fire and Fuel Types

Table 1 summarizes the fuels burnt in each of nine experimental fires. The fuels were selected for the fires with several objectives in mind. There were two fires each of brown ponderosa pine needles (fires 3 and 5) and freshly cut sagebrush (fires 8 and 12), which offered the opportunity to measure separately the products of important fuel components in western United States land management fires, to qualitatively investigate the natural variation in nominally identical fires and, especially from the pine needles, to investigate the temporal behavior of fire emissions in a relatively simple fuel bed.

Many important biomass fires burn in an inhomogeneous mixture of several fuels [*Kauffman et al.*, 1994; *Seavoy*, 1973]. We therefore included preliminary simulations of widely occurring natural and anthropogenic fire types. Two of the fuel beds (fires 9 and 10) contained litter and "duff" (partially decomposed organic matter) and represent attempts to simulate a typical forest-floor ground fire in a coniferous forest. A further common type of wildfire is the crown fire which, along with the ground fuels, consumes the foliage of live, mature trees. A low-intensity crown fire was simulated by fire 11, which featured vertically oriented green pine limbs over a base of litter, dry needles, and small woody fuel. Finally, the two main fire types used to dispose of "activity fuels" (logging waste or harvesting residues also termed "slash") were also simulated. Unpiled, scattered fuels were burned in fire 6, a broadcast burn simulation, and fire 7 simulated burning piled, woody logging waste.

Fuel contents were not systematically determined due to malfunction of the CHN analyzer. Where required in calcula-

Table 1. Fuel Components and Amount Used for Fire-Type Simulations

Fire Type	Number	Fuel Bed Composition	Mass Percent	Comment
Pine needle 1	3	pine needles	100	pinus ponderosa
Pine needle 2	5	pine needles	100	pinus ponderosa
Sagebrush 1	8	sagebrush	100	artemisia tridentata
Sagebrush 2	12	sagebrush	100	artemisia tridentata
Broadcast	6	duff	44	
		pine needles	14	pinus ponderosa
		twigs	18	
		wood	24	
Slash	7	twigs and needles	10	pinus ponderosa
		small branches	90	
Ground 1	9	pine needles	27	pinus ponderosa
		pine needles and duff	73	
Ground 2	10	duff	39	
		twigs and needles	35	pinus contorta
		pine needles	26	pinus ponderosa
Crown	11	twigs and needles	26	pinus contorta
		wood < 30mm	19	pseudotsuga menziesii
		pine needles	19	
		green needles and twigs	36	pinus ponderosa

tions, carbon content is assumed to be the commonly accepted value of 45% of dry matter for all fuels except brown ponderosa pine needles. For this fuel, 51% was assumed based on *Klemmedson* [1975] and a small number of measurements of the composition of subsamples with a Perkin-Elmer 2400 CHN analyzer. The N:C ratio determined from these measurements was 0.6%.

Experiment

The experimental configuration and FTIR spectrometer have been described previously [*Griffith et al.*, 1991] and are shown in Figure 1. The fuel is burned on an ~ 1 x 2 m continuously weighed fuel bed, and the smoke captured by a 1.5-m-diameter stack with a 3.6-m inverted funnel opening just above the fuel bed. A sampling platform surrounds the stack 15 m above the fuel bed. The IR light source was collimated and transmitted twice across the stack through the smoke for a total smoke absorption path of 3 m, then focused and recollimated into an EOCOM interferometer with a Ge/KBr beam splitter and InSb/MCT sandwich detector. Spectra were alternately recorded by the InSb (1800-3900 cm^{-1}) and MCT (700-1900 cm^{-1}) detectors throughout each fire. Resolution was 0.12 cm^{-1}, which is approximately the pressure-broadened full width at half height of individual spectral lines. The spectra recorded before the fire were used to determine background levels of H_2O, CO_2, CO, and CH_4 and to serve as reference spectra to create absorbance spectra from spectra collected during the fire where required. Normally 5-20 scans were coadded over 0.5 to 2 min for each spectrum, with higher time resolution used near the beginning of the fire. Fires typically burnt for about 1 hour, resulting in 25-40 individual spectra per fire.

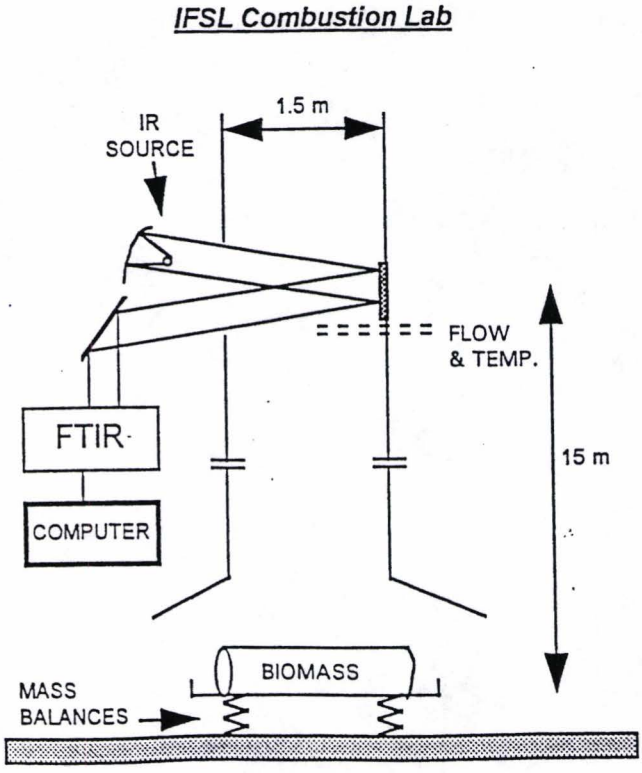

Figure 1. Schematic of the experimental arrangement used to make the measurements.

Mass flow up the stack was measured by a hot wire mass flowmeter (Kurz, model 455). The absolute flowmeter calibration was uncertain, and the flowmeter malfunctioned for fires 9-12, as discussed in more detail below. Temperature was measured by a thermocouple gauge, CO and CO_2 by NDIR (Horiba PIR-2000), and NO and NO_x by chemiluminesence (Thermoelectron model 42). These measurements were logged every 5 s. Samples for auxiliary gas measurements were drawn from the center of the stack near the FTIR beam through ~ 30 m of 0.25" Teflon tube. The fuel bed mass was recorded every 30 s for fires 8 -12. The stack gas flow was driven by convection without additional fan forcing. Normal atmospheric pressure at the IFSL is 90.9 kPa. Temperatures in the stack gas absorption path 15 m above the fuel bed ranged from 300 to 420 K.

Spectrum Analysis

Three different procedures were followed to compute trace gas concentrations from spectra. For most gases, reference spectra were calculated from the HITRAN [*Rothman et al.*, 1992] molecular absorption line parameter database and fitted to the measured spectra using classical least squares (CLS) fitting in selected spectral regions. For species where this was not applicable, either interactive spectral subtraction or peak-height-based analyses using reference spectra were used. The three procedures are briefly described below.

Synthetic Calibration/CLS-based retrievals. The Multiple Atmospheric Layer Transmission (MALT)/CLS method is described in detail elsewhere [*Griffith*, 1996]. Briefly, a set of calibration spectra is calculated from the HITRAN database using the program MALT, such that the calculated spectra closely match real experimental spectra over a range of gas concentrations. These spectra are then used as a calibration set for conventional quantitative analysis using CLS methods [*Haaland*, 1990]. In CLS analysis, measured spectra are fitted by least squares with a linear combination of calibration spectra; all absorbing species are simultaneously fitted. For each trace gas species an optimum small spectral region is selected for the gas or gases of interest. The spectral regions used for each gas are listed in Table 2. For each region a set of calibration spectra, including all molecules absorbing in that region, was calculated at 10 K intervals from 290 to 420 K and the analyses of measured spectra were carried out using calibration spectra calculated at the temperature nearest the measured temperature at the time the spectrum was recorded. Figure 2a shows an example of a MALT/CLS fit to an experimental spectrum for CO/CO_2 at 2211-2243 cm^{-1}.

Spectral subtraction and peak-height-retrievals. For species for which spectral line parameters are not available, MALT/CLS cannot be used and more traditional methods are required. This was the case for CH_3OH, C_2H_4, CH_3COOH, and terpenes. For CH_3OH a prominent *Q*-branch feature appears near 1033 cm^{-1}, overlapped by single lines of NH_3. A calibrated laboratory spectrum of 36.1 parts per million (ppm) CH_3OH in 90.9 kPa N_2 was recorded in a 5.6-m White cell on a Bomem DA3 FTIR spectrometer at 0.12 cm^{-1} resolution and used as a reference for interactive spectral subtraction. The absorption coefficient agreed with that derived from the spectrum of *Hanst and Hanst* [1994] within 10%. A MALT-calculated NH_3 spectrum at the correct temperature was then interactively subtracted from the measured spectrum to remove the NH_3 absorption lines, followed by interactive

Table 2. Spectral Regions Used to Retrieve Concentrations Reported in This Work

Molecule	Spectral Regions or Peaks	Molecule	Spectral Regions or Peaks
H_2O	3020.0 - 3007.1	CH_3COOH	1176[c]
CO_2 and CO	2242.7 - 2210.9	CH_3OH	1033.3[d]
CO_2	737.01 - 727.92	CH_2O	2782.7 - 2777.3
CO_2	2252.8 - 2239.9[a]	HCOOH	1107.4 - 1102.7
CO	2055.8 - 2049.5[b]	NO	1913.4 - 1911.0
^{13}CO	2062.2 - 2061.7[b]	NO	1907.1 - 1905.1
CO	2179.7, 2176.2, 2172.8[a]	NO	1903.8 - 1902.3
CH_4	3020.0 - 3007.1	NO	1901.1 - 1899.9
CH_4	2997.3 - 2976.1	NO	1906.9 - 1899.5
CH_4	1306.7 - 1299.0	NO_2	1599.5 - 1597.7
C_2H_4	949.4[c]	NH_3	1047.3 - 1045.1
C_2H_6	2987.0 - 2985.7	NH_3	968.7 - 961.7
C_2H_6	2984.7 - 2982.7	NH_3	933.5 - 926.5
C_2H_2	3271.2 - 3254.7	HCN	3272.1 - 3270.7
C_2H_2	743.4 - 728.8	SO_2	1348.5 - 1347.7
Monoterpenes	2930[c]	OCS	2071.4 - 2069.9

[a]Stronger peaks used only to quantify background.
[b]Regions used only to spot check the precision.
[c]Analysis based on peak height.
[d]See text for details.

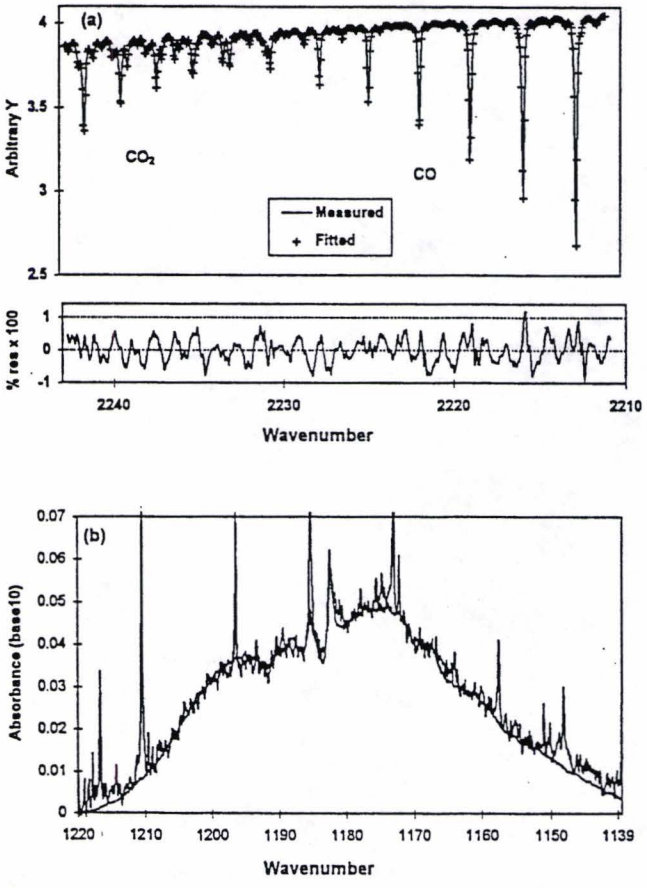

Figure 2. (a) Example of measured, fitted, and % residual (=(fitted-measured)*100) spectra from Multiple Atmospheric Layer Transmission/classical least squares (MALT/CLS) analyses for CO and CO_2. Lines from 2210 to 2235 cm^{-1} are due to CO and lines from 2232 to 2245 cm^{-1} to CO_2. Mixing ratios determined from the spectra are 1558 ppm CO_2 and 175 ppm CO. (b) A smoke spectrum from fire 11 together with a scaled reference spectrum for acetic acid from *Hanst and Hanst* [1994]. The additional sharp lines in the smoke spectrum are due to water vapor. The scaling factor for the reference spectrum and density correction indicate 25.7 ppm acetic acid in the smoke.

subtraction of the reference CH_3OH spectrum. The scaling factor of the CH_3OH spectrum required to subtract the CH_3OH feature from the measured spectrum provided the equivalent CH_3OH concentration.

For C_2H_4 and CH_3COOH the concentrations were based on published reference spectra at appropriate resolution [*Hanst and Hanst*, 1994]. Peak absorption coefficients were determined from the published spectra and applied to peak heights in the measured spectra to retrieve concentrations according to the Beer-Lambert law. For CH_3COOH and C_2H_4 the spectral features are broad but not overlapped by other broad features, and their characteristic shapes and positions provide unambiguous identification. Figure 2b shows an example of a measured spectrum from fire 11 together with a reference spectrum for acetic acid taken from *Hanst and Hanst* [1994].

Auxiliary Data

The CO_2, CO, NO, and NO_x analyzers were calibrated by standard methods using National Institute of Standards and Technology (NIST)-traceable standards. The flowmeter and thermocouple gauge relied on manufacturer's calibrations. To enable comparisons, all data were reduced to a common 1-min time base using a cubic spline interpolation.

Accuracy and Precision of Results

In good quality laboratory spectra (S:N > 1000), absolute accuracy using the MALT/CLS method is normally better than 2% [*Griffith*, 1996], whereas for the spectra here the S:N is typically around 100. Analyses of several species was possible from two or more independent spectral regions (e.g., CO_2, CH_4, NH_3, and C_2H_2). The agreement in replicate measurements of the same species in different spectral regions for most species is better than 5% at concentrations well above the detection limit and this is taken as a general estimate of the accuracy of the MALT/CLS retrievals (including accuracy of the HITRAN absorption cross sections). In addition, there is a typical sensitivity of ~ 1% K^{-1} to assumed temperature. Thus rounding of the analysis temperature to the nearest 10 K (and variation in temperature across the stack of the same order) introduces an additional maximum error of ~ 5%. We

allow a further 4% error for variations in pathlength and background absorption outside the stack due to smoke leakage through the viewing port. In summary, a general estimate of total error in single gas concentration measurements is ~ 8% (1σ) or 1 ppmv, whichever is higher. This implies an accuracy of 11% (1σ) for emission ratios of compounds due to the same combustion process.

For the specific case of H_2O, a significant part (~ 20%) of the total absorption is due to H_2O at room temperature in the 3-m optical path outside the stack. To avoid large errors due to temperature dependence of the absorption line strengths, for the water analysis we used lines in the spectral window near 3010 cm^{-1} which were found to be only weakly temperature dependent.

For some species, comparisons are possible with simultaneous measurements by other instruments. Comparisons of FTIR and non-dispersive infrared (NDIR) measurements of CO and CO_2 show excellent relative agreement but with FTIR measurements systematically ~ 7% higher than NDIR. Similar comparison of NO by FTIR and chemiluminescence show agreement within 10%. For consistency the NDIR and chemiluminescence measurements have not been used in calculating emission ratios or other derived quantities.

Measurement of total mass flow in the stack by the hot wire flowmeter is subject to error due to the inhomogenous flow profile and the absolute flowmeter calibration. The errors in fuel bed mass and temperature measurement are assumed to be negligible relative to those in concentrations and flow.

Derived Quantities

The raw data from each fire consist of time series of concentrations, fuel mass, temperature, and stack gas flow. Concentrations are converted to equivalent mixing ratios at the temperature and pressure of the sample. A number of derived quantities are of use in discussing the following results:

Emission ratio is the ratio of (molar) concentrations of two species, normally as the excess concentrations above background.

Emission factor is the ratio of the amount of a species emitted to the amount of fuel burned in grams per kilogram or moles per kilogram.

Molar emission factor is the ratio of the amount of a particular element in a species emitted to the amount of that element in the fuel burnt, in units of mole per mole. Emission factors are integrated over time and may be defined for the whole fire or for separate fire processes such as flaming and smoldering. Calculation of emission factors from the experimental data is described below.

Combustion efficiency (CE) is the molar ratio of CO_2 emitted to the carbon burned and should be 1.0 for complete combustion. For practical purposes we use modified combustion efficiency (MCE) as the ratio of measured emitted CO_2 to the sum of emitted CO_2 + CO:

$$MCE = [CO_2] / [CO_2 + CO] \quad (1)$$

on the grounds that $[CO_2 + CO]$ correlates well with the total carbon burnt [*Ward and Radke*, 1993]. MCE can be calculated on an instantaneous or time-integrated basis.

Calculation of Emission Factors

The molar emission factor for species x relative to fuel carbon is determined as the molar flow of x up the stack (flow(x)) divided by the molar flow of C in all carbon-containing species up the stack (flow(C)):

$$\text{molar } EF(x) = \text{flow}(x) / \text{flow}(C) \quad (2)$$

The molar emission factor relative to fuel mass (grams dry matter), EF(x), requires the fuel carbon mass fraction, C(fuel):

$$EF(x) = \text{molar } EF(x) \times C(\text{fuel}) / 12 \quad (3)$$

Flow(x) is the product of the total molar flow (determined by the flowmeter) times the mixing ratio of x (determined by FTIR). For flow(C) we take the sum of flows of all measured C-containing species as a close approximation to total C. The molar emission factor for species x times the molecular weight of species x gives the emission factor on a mass ratio basis. This method provides the most reliable emission factors because absolute errors in the flow measurement cancel. It is only important that the relative shape of the flow versus time profile be correct to ensure the correct weightings in calculating time-averaged emission factors.

For fires 9-12 the flowmeter malfunctioned and an independent measurement of flow was required. In principle, the stack flow can also be determined from the measured total fuel mass loss if the fuel composition is known and it is assumed that all smoke is collected by the stack. For fire 8 (sagebrush fuel) both the mass loss and the stack flow were measured and allow an intercalibration of the two methods. Figure 3 shows plots of the integrated carbon loss for fire 8 against time as calculated from both stack flow and from the mass loss, assuming fuel composition of 45%C and 6%H. The flowmeter measurements were scaled by 0.76 to force agreement of the two methods, which provided the effective calibration factor for the flowmeter. The absolute calibration factor so determined may be in error by up to 10% due to the assumption of 45% fuel carbon in the sagebrush fuel. The calibration factor has recently been remeasured in our laboratory to be 0.75 in an independent calibration.

For consistent treatment of all fires, emission factors have therefore been determined from stack flows calculated as follows: For fires 3-7, for which no fuel bed mass data were collected, the measured flow data were used scaled by a calibration factor of 0.76. For fire 8, for which flow and mass

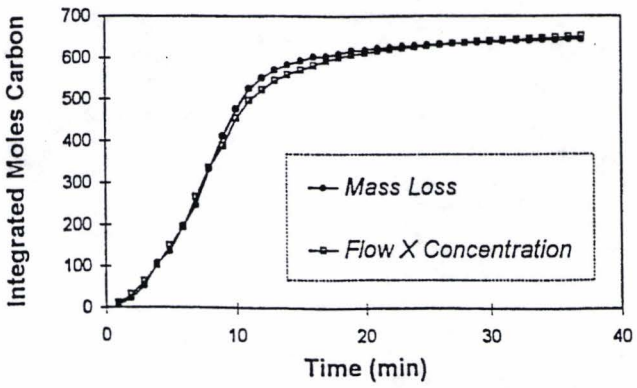

Figure 3. Integrated carbon flow up the stack as calculated from the mass loss record and the concentration times flow data (see text for details).

Table 3. Emission Factors for Flaming and Smoldering Combustion and for the Total Fire (mole/kg dm (x 100)); Relative Production; Modified Combustion Efficiency; and Fuel Consumption by Smoldering Process for Each Fire

Fire Number/ Type	Combus-tion Type	Δ Gas Flaming					Smoldering				Pyrolysis/Distillation								Smoldering Percent		PM2.5
		H_2O	CO_2	NO	NO_2	SO_2	CO	CH_4	C_2H_6	NH_3	C_2H_4	C_2H_2	HAc[a]	MeOH	H_2CO	HFo	HCN	MCE	Process	Phase	g/kg
3/	F[a]	5933	4173	10.6	1.14	2.70	40.36	4.64	0.58	0.09	0.56	0.96	0.41	0.11	1.25	bdl[b]	bdl	0.990	22.6	24.2	
Pine needles	S	3570	3334	0.84	bdl	bdl	656.8	126	17.9	12.8	10.8	2.96	17.1	6.69	3.63	bdl	bdl	0.835			
	T	5384	3986	8.33	0.55	1.55	181.4	29.9	4.07	2.94	2.54	1.45	3.95	1.68	1.80	bdl	bdl	0.956			nd[c]
	R	1	2	5	14	12	3	4	6	8	9	13	7	11	10						
5/	F	5291	4172	8.94	1.33	4.0	42.40	4.62	0.74	0.41	0.87	0.67	0.14	0.22	0.49	bdl	bdl	0.990	18.3	24.5	
Pine needles	S	5487	3275	0.95	0.08	bld	702.1	137	22.5	13.6	11.1	5.74	12.1	3.26	4.75	bdl	bdl	0.823			
	T	5474	4002	7.87	1.22	2.7	166.4	28.2	4.35	2.84	2.64	1.60	4.14	2.03	0.98	bdl	bdl	0.960			30.4
	R	1	2	5	13	9	3	4	6	8	10	12	7	11	14						
6/	F	5684	3701	6.56	1.89	0.68	41.45	2.90	0.56	0.60	1.02	0.88	0.02	0.32	1.43	bdl	bdl	0.989	25.1	45.8	
Broadcast	S	2109	3215	1.67	0.19	0.09	463.1	44.3	6.08	10.6	4.85	1.55	2.19	3.01	2.91	bdl	bdl	0.874			
	T	4722	3577	5.02	1.73	0.67	146.8	15.1	1.93	3.38	2.21	1.15	0.72	0.93	2.25	bdl	bdl	0.961			5.93
	R	1	2	5	10	14	3	4	9	6	8	11	13	12	7						
7/	F	6209	3724	3.82	1.52	1.87	22.59	1.49	0.09	nd	nd	0.68	nd	nd	0.43	nd	bdl	0.994	15.6	23.6	
Slash	S	2977	3170	0.21	0.10	4.95	523.4	38.3	5.01	nd	nd	1.86	nd	nd	4.37	nd	bdl	0.858			
	T	5439	3637	2.93	1.31	1.84	100.5	7.70	0.78	nd	nd	0.86	nd	nd	1.17	nd	bdl	0.973			1.48
	R	1	2	5	7	6	3	4	10			9			8						
8/	F	6827	3654	9.44	2.15	2.60	82.54	4.62	0.28	0.73	1.48	1.66	bdl	bdl	1.46	bdl	bdl	0.978	18.1	70.0	
Sagebrush	S	1320	3267	7.79	0.17	bdl	450.8	18.2	1.74	5.62	2.50	1.26	bdl	bdl	2.47	bdl	bdl	0.879			
	T	5737	3585	9.25	1.66	1.85	149.6	6.67	0.47	1.62	1.61	1.49	bdl	bdl	1.55	bdl	bdl	0.960			2.32
	R	1	2	4	7	6	3	5	12	8	9	11			10						
9/	T	4720	3229	4.07	3.12	4.08	403.8	39.9	6.48	8.67	7.29	3.39	12.3	10.6	9.28	bdl	bdl	0.889	na[d]	na	nd
Ground	R	1	2	12	14	11	3	4	10	8	9	13	5	6	7						
10/	T	5514	3476	5.61	3.12	2.60	212.4	23.4	3.58	7.29	4.09	2.12	4.57	2.51	5.96	bdl	bdl	0.942	na	na	nd
Ground	R	1	2	7	11	12	3	4	10	5	9	14	8	13	6						
11/	T	6404	3279	5.14	1.43	2.16	324.5	56.0	6.64	6.53	11.3	4.96	11.5	9.93	9.18	2.38	1.42	0.910	na	na	nd
Crown	R	1	2	11	15	14	3	4	9	10	6	12	5	7	8	13	16				
12/	F	6151	3671	10.6	2.00	3.11	69.06	3.33	0.28	0.71	1.09	1.19	bdl	bdl	1.64	bdl	bdl	0.982	10.9	20.0	
Sagebrush	S	860.0	3219	4.85	0.31	bdl	513.4	9.40	0.63	4.40	0.59	2.56	bdl	bdl	0.46	bdl	bdl	0.862			
	T	5416	3622	9.81	1.76	2.65	117.2	4.38	0.30	1.13	1.09	1.27	bdl	bdl	1.39	bdl	bdl	0.969			nd
	R	1	2	4	7	6	3	5	12	10	11	9			8						

Each gas is listed with the process that dominates in its formation.

[a]F, flaming; S, smoldering; T, total (fire integrated); R, rank (order of production).

[b]bdl, below detection limit.

[c]nd, no data.

[d]na, not applicable.

[e]HAc, acetic acid; MeOH, methanol; HFo, formic acid.

loss data were forced to agree, flow data scaled by 0.76 were also used. For fires 9-12 the flows implied by the measured fuel mass loss were calculated, assuming 45%C and 6%H, and were used in place of actual flow measurements.

We estimate that the relative weighting of compounds due to the flow profile used in determining fire-averaged emission factors is accurate to 10% (1σ). We estimate the probable error due to assuming the %C as < 10% and that due to unmeasured carbon species as < 2%. In summary the data are presented in compact form as emission factors in Table 3 with an estimated accuracy of 16% (1σ).

Results and Discussion

Time series of concentrations of 14 species could be determined simultaneously for most of each fire. These species were carbon dioxide, carbon monoxide, methane, ethane, ethene, ethyne, formaldehyde, methanol, acetic acid, volatile higher hydrocarbons (terpenes), water, nitric oxide, nitrogen dioxide, ammonia, and sulfur dioxide. Three others, formic acid, hydrogen cyanide, and carbonyl sulfide, were measurable only during periods of peak emissions for some fires. Emission factors and modified combustion efficiency for each fire are summarized in Table 3, which includes these quantities for the whole fire as well as by fire process as described in the ensuing discussion.

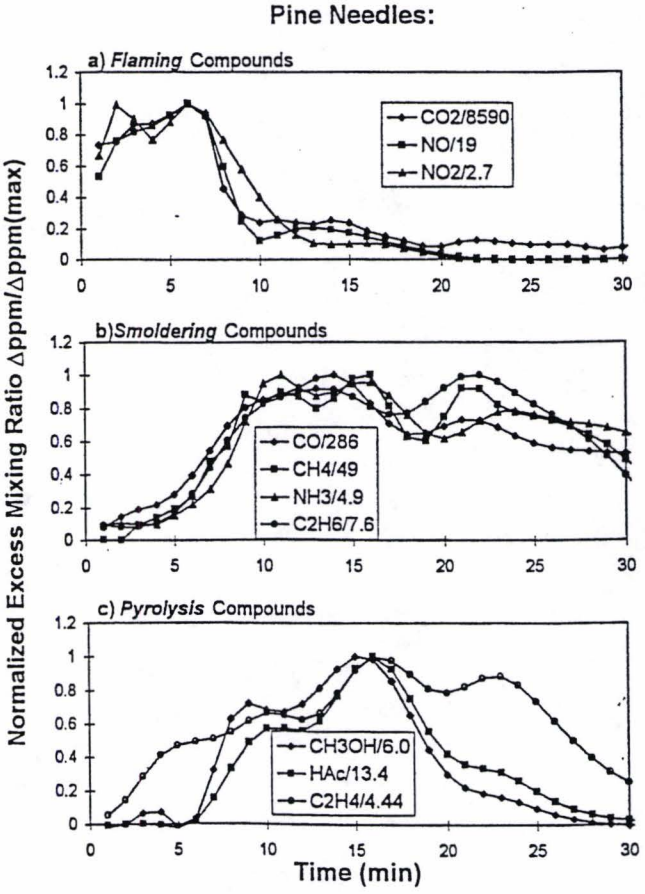

Figure 4. Examples of time evolution of compounds emitted from a fire in a fuel bed of pine needles (fire 5), separated by (a) flaming, (b) smoldering, and (c) pyrolysis/distillation combustion process.

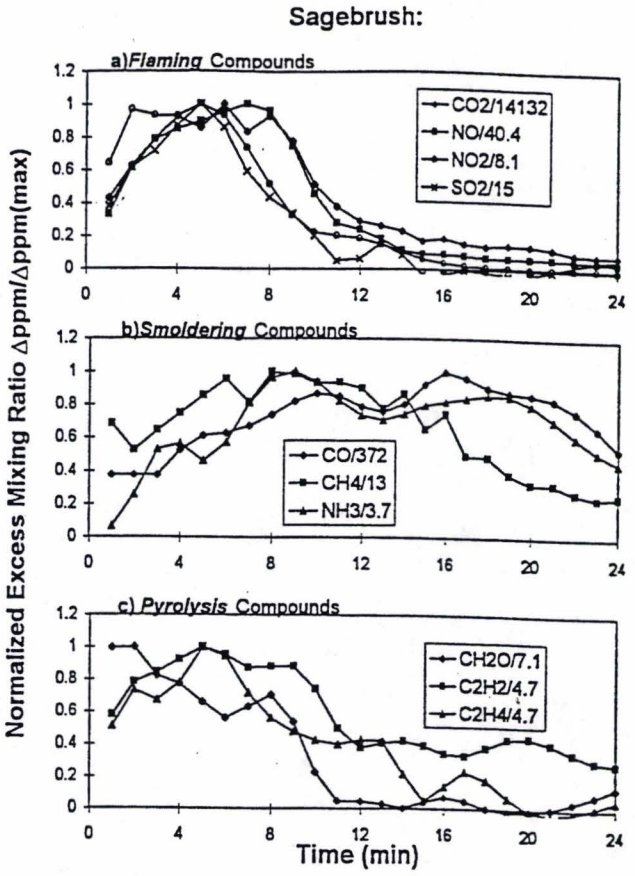

Figure 5. As for Figure 4 except for whole sagebrush fuel (fire 12).

Temporal Behavior of Fire Emissions

Earlier laboratory studies of *Lobert et al.* [1991] were carried out in homogeneous, well-characterized fuels. That work demonstrated that some compounds can be attributed to flaming or smoldering combustion based on a linear correlation with CO_2 or CO, similarity of the normalized temporal profile with CO_2 or CO, and degree of oxidation. Our results confirm some of these observations. The normalized temporal profiles for selected flaming and smoldering compounds can be seen in Figures 4-6 (part a and b) for fires burning in dry brown pine needles (fire 5), sagebrush (fire 12), and a homogeneous mixture of forest residues (fire 6).

We also measure significant amounts of compounds that do not correlate linearly with either CO_2 or CO and show markedly different normalized temporal profiles. The temporal profiles for some of these compounds can be seen in Figures 4-6 (part c). These compounds are principally unburnt pyrolysis products originating from heating of the primary fuel [*Shafizadeh et al.*, 1976; *Overend et al.*, 1985; *Evans et al.*, 1986; *DeGroot et al.*, 1988; *Cofer et al.*, 1989]. Pyrolysis products that we measure are acetic and formic acid, methanol, formaldehyde, and light unsaturated hydrocarbons. In studies limited to the emissions from smoldering combustion, the entrainment of unoxidized pyrolysis compounds in the smoke naturally falls within the definition of smoldering combustion [*McKenzie et al.*, 1995]. However, in this work these compounds also occur in the emissions during times dominated by flaming combustion. (See Figures 4 - 6.) Therefore because production of these compounds exhibits poor tempo-

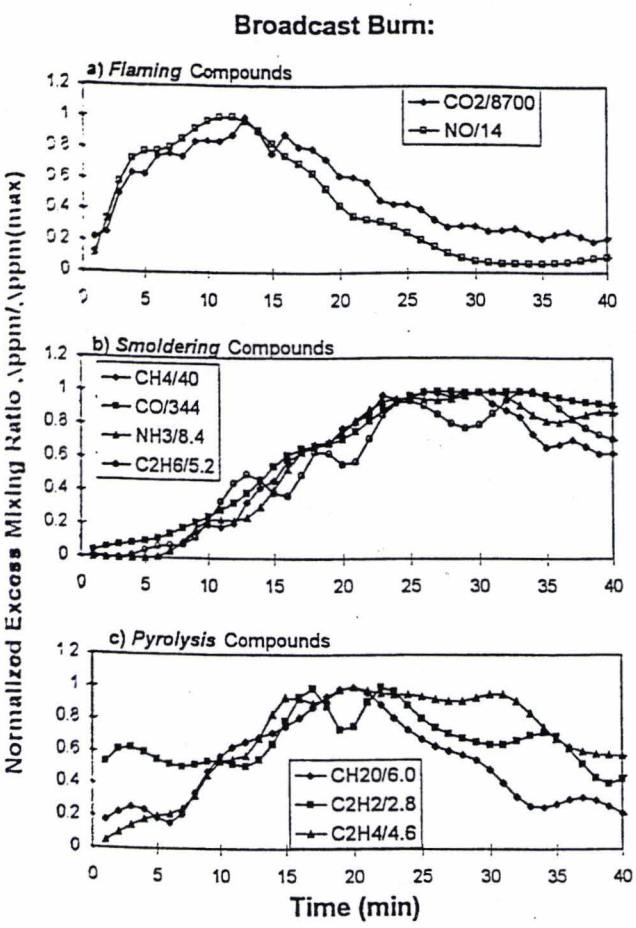

Figure 6. As for Figure 4 except for a simulated broadcast burn (fire 6).

ral correlation with both CO and CO_2 and because they may primarily be formed by thermal "cracking" of biomass without the reaction of an atmospheric oxidant with the fuel, we adopt an operational definition of smoldering combustion that excludes these compounds and invoke one further category of compounds: the "distillation and pyrolysis" category. We recognize that the construct of a category or class of compounds is a simplification and that there may be some overlap. For example, most of the CO_2 is produced by flaming combustion, but CO_2 is also the major product of smoldering combustion. Smoldering compounds correlate well with CO, which can be produced by direct, thermal decarbonylation of biomass, by gasification of char, or by incomplete oxidation of other emissions in flames. Formation of methane is a high-temperature pyrolysis process, and formaldehyde can be formed pyrolytically or from the partial oxidation of methanol or methane. Examples of fire processes which generate emissions but do not involve flames are diagrammed in Figure 7 [*Lephardt and Fenner*, 1980; *Overend et al.*, 1985; *Jakab et al.*, 1993]. These processes create the emissions in our smoldering and pyrolysis/distillation categories and also create the fuel that drives the turbulent diffusion flames that produce the bulk of the emissions.

The pyrolysis compounds do not always track with each other or with any single tracer species because they often originate from different precursors or in different thermal or moisture regimes and because heat production and combustion efficiency vary throughout a fire. On the other hand, correlations among pyrolysis compounds may identify common precursors or thermal regimes. An example is shown in Figure 8 where two pyrolysis compounds, methanol and acetic acid, are highly temporally correlated in nearly a 1:1 molar ratio for three different fires. The 1:1 production is in contrast to the 1:2 production observed for brown pine needles (Figure 4c). Consideration of the temporal profiles and production ratios suggests that methanol and acetic acid may be produced from biomass in similar thermal regimes (relatively low temperature, as shown in Figure 7) but from different precursors.

Interpretative model. From the perspective of being able to monitor total fire emissions for many species continuously, we find that the concept of fire stages or phases separated in time is less useful than the more general concept of fire processes, which may coexist in time. These processes are summarized in the following paragraphs. Figure 9 presents plots of modified combustion efficiency versus time for fires 3 (pine needles) and 6 (broadcast simulation) which is useful in interpreting the different processes.

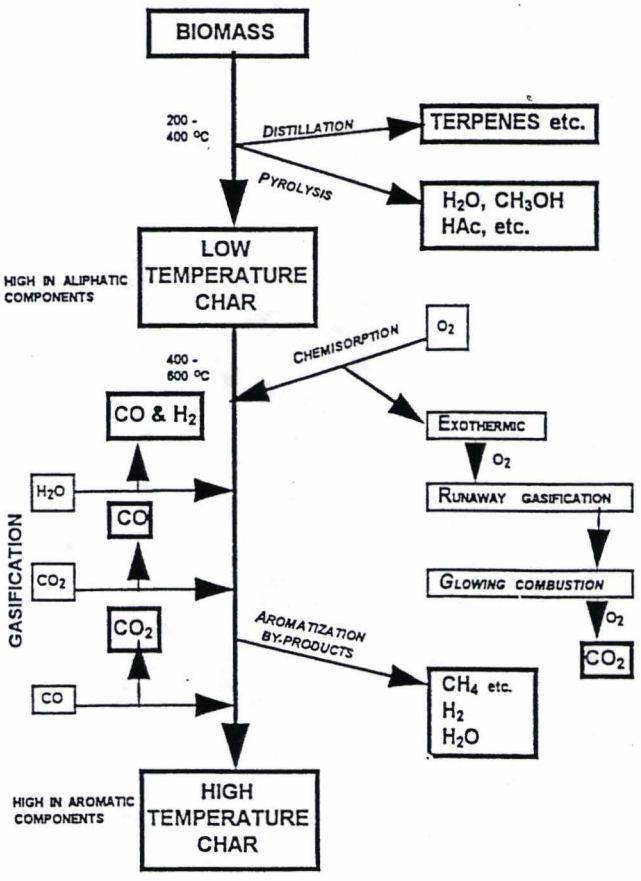

Figure 7. Some of the important nonflaming processes in biomass combustion are summarized pictorially. Initially, heating of biomass releases distillation products such as terpenes and oxygenated pyrolysis products such as water and acetic acid. This contributes to the formation of low temperature char. Continued heating at increased temperatures releases hydrocarbons forming high temperature char. The high temperature char participates in gasification and glowing combustion producing the indicated emissions. The emissions shown here can form a flammable mixture. The rate of heat transfer from the flames and surface oxidation to the solid fuel controls the rate of production of the gaseous fuel for the flames.

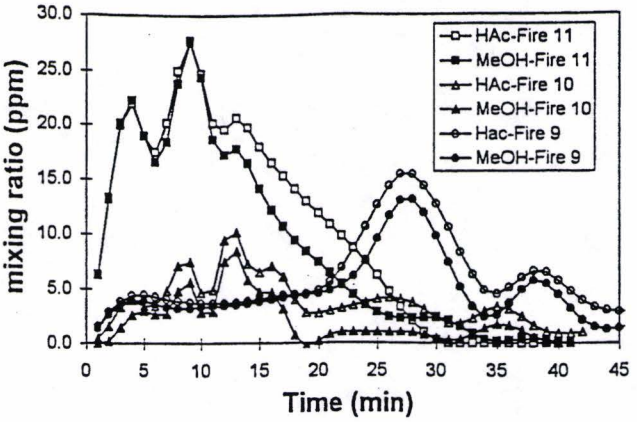

Figure 8. Temporal profiles for the concentration of acetic acid and methanol in parts per million from a selection of fires.

For a homogeneous or well-mixed fuel bed a typical fire behaves as follows:

1. Following ignition at one end of the fuel bed, the flames and an associated pyrolysis/distillation zone begin to expand across and down through the fuel bed. After a few minutes the entire bed gives rise to 1- to 3-m flames for several minutes and the emissions are dominated by the products of flaming combustion with a comparably minor contribution from unmodified pyrolysis products. During this time the fire burns with high (typically 99%) combustion efficiency. This behavior corresponds to the first 10 min in the simulated broadcast burn (Figure 9a) and the first 5 min of the pine needle fire (Figure 9b).

2. At the ignited end, the flaming zone starts to shift toward intermittent pockets of smaller flames mixed with "smoldering" combustion. Chemisorption of O_2 on char is exothermic and drives glowing combustion which provides heat to pyrolyze and "distill" adjacent fuel which, in turn, contributes to more char formation. CO_2, CO, and hydrocarbons are released from the char. With less flaming, a larger fraction of distilled and pyrolytically formed compounds can be entrained in the smoke unoxidized. As the shift toward smoldering and pyrolysis propagates across the fuel bed the combustion efficiency drops with time. This behavior is illustrated in the midsection of Figure 9a. Especially during this transition period of the fire, the emissions are the products of all three processes.

3. After the flames have ceased over the entire fuel bed the products are dominated by smoldering but still with an important contribution to emissions from pyrolysis. During this time the combustion efficiency is observed to range from 80 to 88% until the fire ceases to burn. This second sustained level of combustion efficiency is seen at the end of both fires in Figure 9.

Emissions from flaming and smoldering peak with the maxima in flaming and smoldering combustion, but peaks in the production of pyrolysis products are more variable. The high heat release rate associated with flaming combustion may pyrolyze more fuel and there is often a peak in the measured pyrolysis products either before, during, or shortly after the peak in flaming products. However, the majority of the initial pyrolysis products would normally be oxidized in the presence of vigorous flaming. During smoldering combustion the pyrolysis products may be made at a lower absolute rate, but they have a higher probability of escaping the flames to be detected in the smoke. Therefore in all fires the quantity of pyrolysis products detected per unit fuel consumption is always higher during times dominated by smoldering combustion. For a specific, homogeneous fuel the flaming and smoldering processes tend to produce smoke that is approximately of fixed relative composition, so that the ratio of highly oxidized compounds to CO_2 is more or less constant from flaming combustion, and the ratio of certain incompletely oxidized compounds to CO is roughly constant for smoldering combustion for a specific fire type. (See Figures 4 - 6 (part a and b).) This is the basis for the observation of "tracking," in which the normalized concentration profiles for flaming or smoldering compounds show a high degree of correlation with the other compounds in the same class [*Lobert et al.*, 1991]. In fires that exhibit tracking it is meaningful to report the ratio of the concentrations, obtained from a spot measurement and for two compounds from the same class, as an approximate emission ratio for the fire as a whole. This is useful because it allows reliance on data which are not fire-integrated to derive emission ratios. Thus in such fires the emission ratio for two compounds that are either both from flaming or both from smoldering can be measured at nearly any time. However, even for a homogeneous fuel bed, where tracking occurs for flaming and smoldering compounds, the pyrolysis products do not all track a single tracer species well. This implies that an integrated sample or (preferably) real-time, continuous sampling of the emissions and the smoke velocity is necessary to obtain good emission factors for these compounds.

When spotty or layered (inhomogeneous) fuel beds are burned, tracking is not observed even for flaming or smolder-

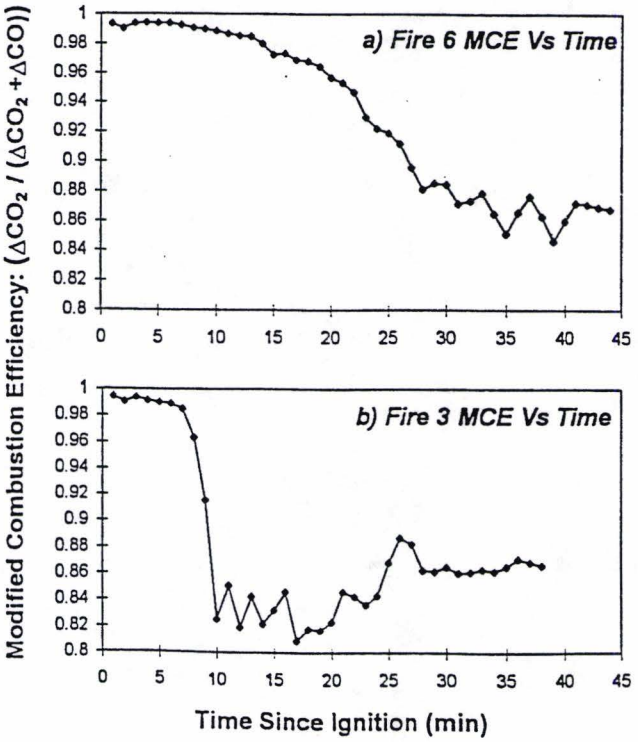

Figure 9. Modified combustion efficiency versus time for (a) fire 6 (broadcast simulation) and (b) fire 3 (pine needles), illustrating two different trajectories important in land management fires.

ing compounds. As different fuels dominate fuel consumption during the course of the fire, the tracking may go away. An example of this type of temporal behavior is shown in Figure 10 which shows the ratio of CH_4/CO during fire 11. During this fire the ratio changes by a factor of 5 from an initial value of 0.2, which is characteristic of pine needles which burn early in the fire, to a value of 0.04 which is characteristic of woody material. In practice, virtually all real fires run in such complex fuel beds, the one possible exception being pure grassland fires. A general approach to quantifying fire emissions is thus preferred, in which time-resolved concentrations and flow are measured and integrated to obtain total emissions.

Relative fuel consumption by various combustion processes. Because the three major fire processes produce different products, it is of use to be able to estimate the fuel consumption by process. Flaming and smoldering would normally account for most emissions by mass, but pyrolysis is important from an emissions standpoint because the sum of its products is similar to total methane emission. Essentially 90-99% of the fuel carbon is converted to either CO_2 or CO from flaming and smoldering. Therefore for the purposes of estimating fuel consumption by process, we make the arithmetic approximation that all the fuel consumption is due to flaming or smoldering combustion. During the initial stages of a fire, emissions are dominated by flaming combustion and we may measure the emissions of nearly pure flaming combustion. For many fires it is also true that near the end of the fire the emissions are dominated by smoldering combustion and we can measure the products of this process. For each fire that featured time periods dominated by pure flaming or smoldering combustion we have computed the emissions per unit amount of fuel for those pure processes. By also quantifying the average emissions per unit amount of fuel for the whole fire, we can then determine the relative importance of each process in consuming fuel in an accurate manner following *Ward and Radke* [1993]. For smoldering

$$\%S = \frac{[EF(\text{flame}) - EF(\text{total})]*100}{[EF(\text{flame}) - EF(\text{smolder})]} \quad (4)$$

We can calculate the percentage fuel consumption by smoldering combustion (%S) for each species individually. For CO_2 and CO, which are measured with excellent S/N throughout the entire fire, the agreement is usually within 1%. For other flaming or smoldering emissions there is also normally good agreement. However, if the emitted species is a distillation or pyrolysis product, for example, methanol, formaldehyde, acetic or formic acid, good agreement is not normally found using such an analysis based on only flaming and smoldering.

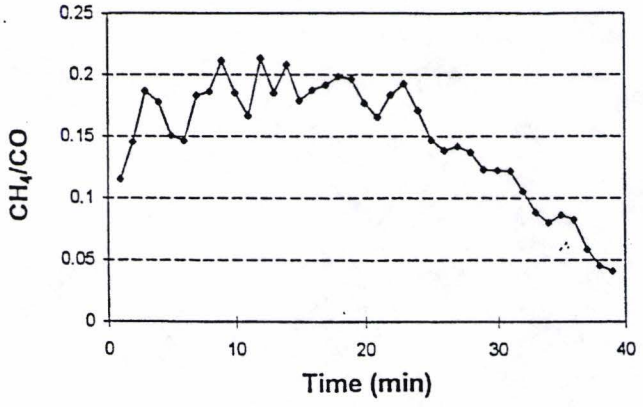

Figure 10. Data from fire 11, illustrating smoldering compounds appearing in a nonconstant ratio over the course of a burn in a heterogeneous fuel bed.

Emission factors and combustion efficiencies for examples of nearly pure flaming and smoldering processes, and the percent fuel consumption by smoldering combustion determined as above, are included in Table 3 for all applicable fires. For the compounds listed as in the pyrolysis/distillation category the total emission factors are more accurate than the process emission factors.

We can contrast our process approach to that of *Lobert et al.* [1991] which distinguishes flaming and smoldering phases in time. In Lobert's work, CO is considered a tracer for smoldering combustion and the time of maximum rate of increase of CO emission is taken as the beginning of the smoldering stage. The results from the two approaches are compared for each fire as entries in Table 3. We find that the calculated fuel consumption for a "smoldering phase" is larger than the calculated fuel consumption by a smoldering process. The agreement between the two approaches is best when the fire makes a rapid transition between periods dominated by the two types of combustion, as in fire 3 (see Figure 9b). The difference between these approaches is more significant to understanding the combustion chemistry than it is in emission estimates. In emission estimates the fuel consumption by a smoldering "phase" may be overestimated, but in these cases, the emission factor for a smoldering "phase" will be underestimated and the resulting emission estimate should be nearly the same.

Production of Oxygenated Organic Compounds

The oxygenated organic compounds measured in this work are formaldehyde, methanol, and acetic acid, with appreciable amounts of formic acid in one fire. Our data are included in Table 3 and plotted as emission factors versus modified combustion efficiency in Figure 11. To date, relatively little information has been available on the direct fire emissions of these difficult to measure compounds, but it is possible to make a limited comparison between our measurements and results obtained earlier. *Cooper* [1980] reports molar emission factors in the range 1- 5 x 10^{-4} moles total aldehyde production per mole C burnt from residential firewood combustion with formaldehyde accounting for most of this. In our six most comparable fires (3,5,6,7,8,12), in which most of the fuel consumption was due to flaming combustion, we report a median molar emission factor of 4.0 x 10^{-4} for formaldehyde. *Hurst et al.* [1994a] sampled Australian savanna fires from aircraft followed by laboratory matrix isolation-FTIR analysis and report average molar emission factors of (2.0± 1.2) x 10^{-4} for formaldehyde and (5.5 ± 3.4) x10^{-4} for acetaldehyde. The field study of *Griffith et al.* [1991] reports much higher levels of formaldehyde with an emission ratio $\Delta CH_2O/\Delta CO_2$ of 2.2 x 10^{-3}, corresponding to an emission factor of ~ 1.9 x 10^{-3}. The field study probed mainly smoldering combustion. The present laboratory study featured two ground fire simulations dominated by smoldering combustion (fires 9 and 10) and for these fires our average molar emission factor for formaldehyde was comparable at 2.0 x 10^{-3}. In summary, there is broad

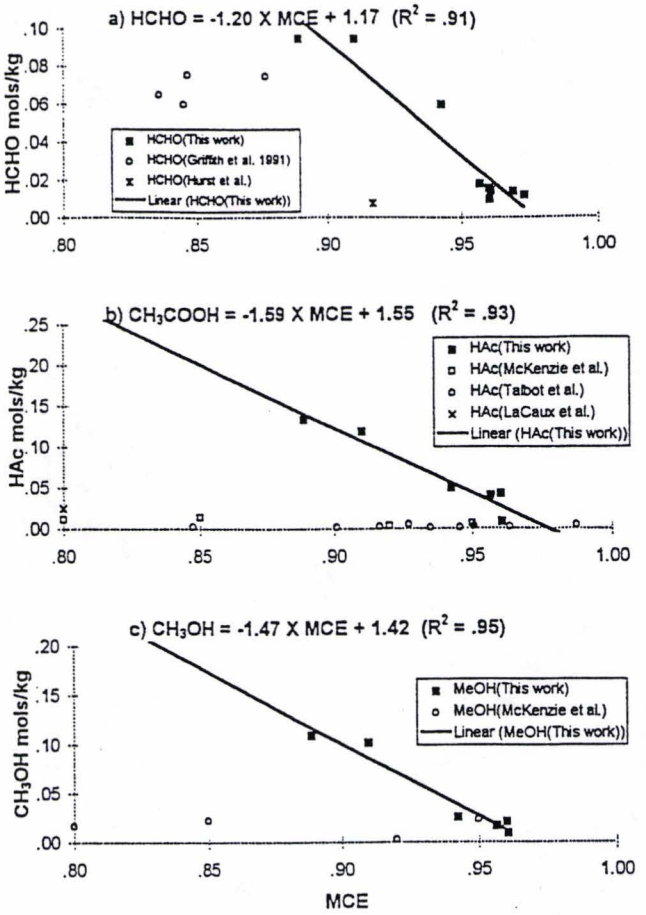

Figure 11. Fire-integrated emission factors as a function of fire-integrated modified combustion efficiency for (a) formaldehyde, (b) acetic acid, and (c) methanol. The regression equations are fit to the results of this study. The results of *Hurst et al.*, *Talbot et al.*, and *Lacaux et al.* are from different (hardwood) fuel types.

agreement, but detailed comparisons are limited by the lack of data on fuel composition and combustion efficiencies from other studies. There are significantly higher quantities of CH_2O emitted from smoldering fires.

For the other oxygenated organics, methanol, acetic acid, and formic acid, few comparisons with other work are possible. *McKenzie et al.* [1995] measured methanol and acetic acid from laboratory fires with coniferous fuels by cryotrapping and gas chromatography/mass spectral (GC/MS) analysis, while three other studies used the mist chamber technique [*Cofer et al.*, 1985] for organic acids: *Talbot et al.* [1988] from brush and hardwood fuels in laboratory studies, *Dinh et al.* [1991] from African savannah fires, and *Lacaux et al.* [1994] from African charcoal-making kilns. In summary our data consistently show good internal consistency with strong correlations of emission factors with combustion efficiency (Figures 11b and 11c) while all other measurements show much lower emission factors and little or no correlation with combustion efficiency. Where sufficient auxiliary data are provided from other studies to estimate combustion efficiencies, these other data are also included in Figure 11. However, the comparison must be treated with caution because in the estimates of (fire averaged) combustion efficiency from other studies there were sometimes insufficient data to weight the flaming and smoldering processes correctly. Correction for this may increase the combustion efficiencies from some other work by ~ 4%.

It is notable that in our sagebrush fires, acetic acid was below the detection limit, which is more consistent with other studies. We measure formic acid in only one fire (the crown fire simulation) at levels 2 orders of magnitude higher than those measured by *Talbot et al.* [1988]. In all studies, acetic acid is emitted at 3-10 times the rate of formic acid. Qualitatively, the oxygenated organic compounds shown in Figure 11 are each emitted at levels about 20 to 25% that of methane and taking into account unmeasured higher homologues, the sum of oxygenated organic emissions may be of the same order as methane emissions.

The discrepancies between studies may be due to the different fuels burned, to the different sampling methods, and to different data analysis methods as discussed above. Direct intercomparisons are required to elucidate these differences. In particular, the present FTIR method is nonintrusive with no risk of losses during sampling. Clearly, our results imply potential for much higher emissions of oxygenated organic species than all previous work. The emissions of these compounds and their effects on regional atmospheric chemistry will be important and should be better understood.

The production of oxygenated organic compounds in fires is of potential atmospheric significance for several reasons: (1) Many of these compounds are reactive. (2) Organic acids contribute significantly to rain and cloud water acidity in remote regions [*Keene and Galloway*, 1984a, b]. (3) Oxygenated organics such as CH_2O may serve as precursors for organic acids such as formic acid and for oxidants such as HO_2 and OH radicals. The atmospheric chemistry of oxygenated organics has been summarized elsewhere [*Finlayson-Pitts and Pitts*,1986]. We note that oxidation of methanol can be a formaldehyde source, that oxidation dominates photolysis as a formaldehyde sink in "moderately polluted conditions," and that oxidation of formaldehyde can produce formic acid. Thus we speculate, as have *Andreae et al.* [1988], that some emitted oxygenated organics may contribute to a secondary gas phase formic acid source. In addition to this, a further secondary source of formic acid could be the oxidation of the emitted alkenes [*Arnts and Gay*, 1979; *Finlayson-Pitts and Pitts*,1986]. Alkenes detected in this work are ethene and possibly monoterpenes [*Yokelson et al.*, 1995]. *Helas et al.* [1992] suggested that volatilized biogenic compounds from biomass burning may be a source of formic acid.

Production of Reactive Nitrogen-Containing Compounds

The dominant measured nitrogen-containing species emitted are NO and NO_2 from flaming and NH_3 from smoldering combustion (see Figures 4-6). If the N:C ratio of the fuel is known, a nitrogen mass balance can be calculated. This was measured only for some subsamples of brown pine needles, with a value of 0.6% as described earlier. For fires 3 and 5 in pine needles, the emission factors for NO, NO_2, and NH_3 average 0.081, 0.0089, and 0.029 mole kg^{-1} accounting for 38%, 4%, and 13% of the fuel nitrogen, respectively, a total of 55%. Emitted N_2O and CH_3CN were below detection limits, and other nitrogenous compounds such as HCN were observed only in the crown fire simulation. Accepting the value of *Kuhlbusch et al.* [1991] of 36 ± 13% for N_2 emission and a value of 10% for ash nitrogen [*Hurst et al.*, 1994b; *Crutzen*

and Andreae, 1990], these emission factors account for all the fuel nitrogen within the experimental uncertainties. These findings are in general agreement with *Hurst et al.* [1994a, b] who report high levels of for NO, NO_2, and NH_3 and that N_2O, HCN, and CH_3CN each account for less than 1% of the fuel nitrogen.

Our data confirm the earlier observation of *Griffith et al.* [1991] that NO_x dominates the measurable nitrogen release during flaming combustion and that NH_3 is the dominant measured N product in smoldering combustion. Early estimates of NH_3 production from biomass burning project NH_3 production be about one third of NO_x production [*Crutzen and Andreae*, 1990]. The laboratory studies of *Lobert et al.* [1991] yielded an average value for NH_3/NO_x of 0.57. Figure 12 shows the fire-integrated NH_3/NO_x ratio from several studies as a function of modified combustion efficiency. At combustion efficiencies below about 0.91 the molar ratio of NH_3/NO_x exceeds unity. The field measurements of *Griffith et al.* [1991], which were biased to smoldering combustion, yield a high average NH_3/NO_x ratio of 3.7. The data of *Hurst et al.* [1994a, b], from aircraft sampling of Australian savanna fires, give a NH_3/NO_x value near 1.1. Taken together, these results suggest that biomass burning may be a more significant source of atmospheric ammonia than has been generally recognized.

Over 50% of the fuel nitrogen is emitted as NO_x or NH_3. The atmospheric chemistry of ammonia is poorly understood, but it is important as the only common water-soluble base in the atmosphere and could potentially neutralize organic and inorganic acids in the plume in the liquid or gas phase. There are indications that a significant fraction of the emitted ammonia may be converted to ammonium ion [*Andreae et al.*, 1988a], but only a small fraction of the formic and acetic acid present in plumes appears to be converted to formate or acetate [*Talbot et al.*, 1988; *Andreae et al.*, 1988b]. NO and NO_2 are catalysts for regional ozone production and precursors for nitric acid production.

Comparison of Laboratory and Field Data

Comparison with FTIR field data from our earlier study [*Griffith et. al.*, 1991] is illustrated for formaldehyde above.

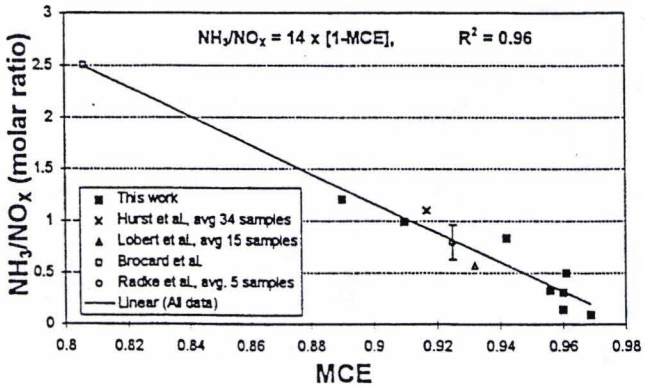
NH3/NOx = 14 x [1-MCE], R² = 0.96
NH3/NOx (molar ratio)
MCE
This work
Hurst et al., avg 34 samples
Lobert et al., avg 15 samples
Brocard et al.
Radke et al., avg. 5 samples
Linear (All data)

Figure 12. Fire-integrated NH_3/NO_x molar ratios as a function of modified combustion efficiency for all fires in this work compared with other studies. *Radke et al.* [1990] report a mass of NO_x, which is represented as a 50:50 mixture of NO and NO_2 and the error bar shows the range of possible values due to changing this ratio.

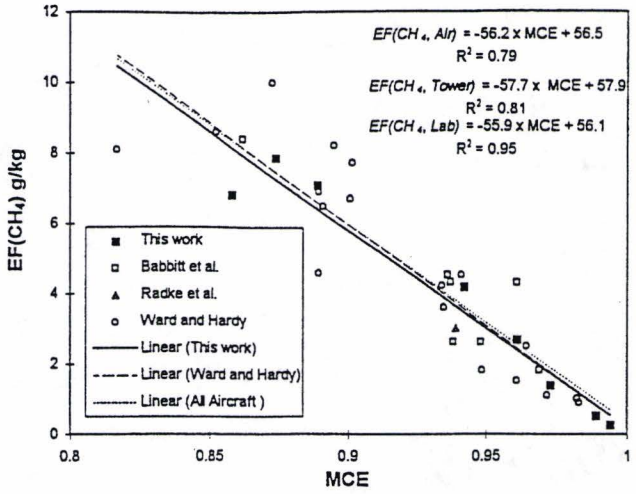

Figure 13. Laboratory results from this work coplotted with comparable field measurements of methane emission factors versus modified combustion efficiency. The comparison is limited to similar pine-dominated coniferous fuels. For the purposes of this figure, the emission factors from this work were calculated assuming 50% C (instead of 45%) as was done in the other three studies.

However, detailed comparison is difficult because of differences and uncertainties in fuel burned and in the relative amounts of different combustion products (i.e., flaming, smoldering, and pyrolysis) sampled. Tower-based sampling which is integrated over the duration of a fire in the field and accompanied by vertical velocity measurements, or aircraft sampling which effectively integrates combustion products from all fire processes in a mixed plume, should provide better comparisons. Figure 13 compares CH_4 emission factors versus MCE from this study of simulated field fires in mixed coniferous fuels (fires 6, 7, 9, and 10) with canister data sampled from aircraft [*Radke et al.*, 1991; *Babbitt et al.*, 1995] and towers [*Ward and Hardy*, 1991] in all cases for mixed coniferous fuels. The agreement is excellent within the limitations imposed by the different sampling and analysis methods.

Emission of Sulfur Compounds

We consistently observe SO_2 emitted from flaming combustion with a mean SO_2/CO_2 ratio of $(7.3 \pm 3.0) \times 10^{-4}$ (1σ). Comparison with other measurements is made difficult by the wide possible ranges of fuel sulfur contents (S:C ratios from 0.023 to 0.9%) [e.g., *Cook*, 1993; *Bowen*, 1979] and the fraction of fuel sulfur volatilized (35-85%) [*Ward et al*, 1982; *Cook*, 1993; *Delmas*, 1982]. These ranges suggest total sulfur/CO_2 emission ratios from 8×10^{-5} to 8×10^{-3}, and published measurements all fall in this range [e.g., *Hurst et al.*, 1994; *Crutzen and Andreae*, 1990; *Andreae et al.*, 1988; *Delmas*, 1982]. We observed OCS only at low levels (<1 ppm) in one fire, consistent with other findings that OCS accounts for only a very small fraction of fuel sulfur [*Crutzen et al.*, 1979, 1985; *Crutzen and Andreae*, 1990; *Ward et al.*, 1982]. There are probably other significant sulfur-containing emissions that were undetected. Consideration of sulfur phytochemistry [*Richmond*, 1973] suggests that hydrogen sulfide, methyl mercaptan, and dimethyl sulfide are likely to be in this class, but they are very weak absorbers of IR radiation.

Conclusions

This work establishes the open-path FTIR technique as a valuable diagnostic tool for continuous, real-time analyses of many gases in smoke, providing an improved understanding of smoke composition and chemistry, fire behavior, carbon and nitrogen cycles, and biomass burning impacts on atmospheric chemistry. The observations in this study with the most relevance to projecting impacts on atmospheric chemistry are summarized as follows:

1. The concept of dividing a large fire into two stages separated in time is insufficient to categorize the temporal behavior of the emissions. There are at least three "processes" that should considered, namely flaming, smoldering, and pyrolysis/distillation. One consequence of this is that a representative sample cannot always be taken at any arbitrary time during a fire. To measure, for example, oxygenated organics or any compound from heterogeneous fuels requires continuous sampling along with flow measurements or isokinetic integrated sampling to weight the relative contributions of the different combustion processes correctly. Only for simple, homogeneous fuels do many compounds "track" one another throughout a fire and allow representative single samples to be collected.

2. Although a lot is known about the combustion chemistry of light alkanes, the gaseous fuel that supplies flaming combustion of biomass is likely to contain large amounts of volatile plant constituents and oxygenated organics. The combustion chemistry of these materials is less well understood and will influence the emissions. The simplest example of this is that the smoke from biomass fires may contain levels of unburnt oxygenated organics and volatilized biogenic compounds that are high enough to have a significant impact on local and regional atmospheric chemistry. The emission levels and their impacts deserve more attention than they have received to date.

3. There is increasing evidence that the fate of nearly all the fuel nitrogen may be accounted for by NO, NO_2, NH_3, N_2, and ash and that of these quantities the amount of NH_3 is likely to be more significant than previously assumed, especially for fires with low combustion efficiency.

4. Determination of integrated emissions from real fires in the field by application of emission factors determined from laboratory studies depends on determining the relative importance of the flaming, smoldering, pyrolysis, and distillation combustion processes (or at least the combustion efficiency) in the real fire.

Acknowledgments. The authors would like to thank Bill Mankin for the use of the FTIR spectrometer, staff of the IFSL for support in measurements and informative discussions; Ron Susott, Ron Babbitt, Gerald Olbu, Patrick Boyd, and Lynn Weger, Andy McCann of Ontar Corporation, for assistance in blending databases, Aaron Goldman for providing molecular parameters for formic acid and ethene, and Geoff Richards, Bill Herget, and Rei Rasmussen for informative discussions. This research was supported in part by the USFS RJVA93847.

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(Received September 2, 1995; revised February 29, 1996;
accepted June 6, 1996.)

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. D15, PAGES 18,865–18,877, AUGUST 20, 1997

Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy

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Abstract. Biomass samples from a diverse range of ecosystems were burned in the Intermountain Fire Sciences Laboratory open combustion facility. Midinfrared spectra of the nascent emissions were acquired at several heights above the fires with a Fourier transform infrared spectrometer (FTIR) coupled to an open multipass cell. In this report, the results from smoldering combustion during 24 fires are presented including production of carbon dioxide, carbon monoxide, methane, ethene, ethyne, propene, formaldehyde, 2-hydroxyethanal, methanol, phenol, acetic acid, formic acid, ammonia, hydrogen cyanide, and carbonyl sulfide. These were the dominant products observed, and many have significant influence on atmospheric chemistry at the local, regional, and global scale. Included in these results are the first optical, in situ measurements of smoke composition from fires in grasses, hardwoods, and organic soils. About one half of the detected organic emissions arose from fuel pyrolysis which produces white smoke rich in oxygenated organic compounds. These compounds deserve more attention in the assessment of fire impacts on the atmosphere. The compound 2-hydroxyethanal is a significant component of the smoke, and it is reported here for the first time as a product of fires. Most of the observed alkane and ammonia production accompanied visible glowing combustion. NH_3 is normally the major nitrogen-containing emission detected from smoldering combustion of biomass, but from some smoldering organic soils, HCN was dominant. Tar condensed on cool surfaces below the fires accounting for ~ 1% of the biomass burned, but it was enriched in N by a factor of 6 - 7 over the parent material, and its possible role in postfire nutrient cycling should be further investigated.

Introduction

Biomass burning emissions are well-established as a significant influence on the atmosphere [*Crutzen and Andreae*, 1990; *Crutzen and Carmicheal*, 1993; *Prather et al.*, 1994; *Prather and Logan*, 1994]. Flaming combustion of biomass fuels primarily produces highly oxidized compounds such as CO_2, NO_x, and SO_2. What is commonly called "smoldering combustion" can be a complex mix of fuel pyrolysis (thermal decomposition of fuel), small flames, and glowing combustion of char. These processes can accompany flaming or occur in varying combination after flaming and produce many less-oxidized gaseous emissions of considerable interest to atmospheric chemists [*Lobert et al.*, 1991; *Yokelson et al.*, 1996a]. Grasses and tropical broadleafed trees are the predominant biomass fuels globally [*Crutzen and Andreae*, 1990]. Flaming combustion accounts for most of the fuel consumption in grass fires. However, the emissions from smoldering combustion in grass fires also play an important role in tropical dry season tropospheric chemistry [*Connors et al.*, 1996; *Thompson et al.*, 1996; *Chatfield et al.*, 1996; *Crutzen and Carmichael*, 1993; *Granier et al.*, 1996]. In fires in tropical and temperate forests, a much larger percentage of the fuel consumption is by smoldering combustion [*Ward et al.*, 1992; *Susott et al.*, 1991], and thus smoldering emissions strongly impact the dry season troposphere in tropical deforestation regions [*Connors et al.*, 1996; *Chatfield and Delaney*, 1990; *Richardson et al.*, 1991; *Keller et al.*, 1991; *Crutzen and Carmichael*, 1993; *Granier et al.*, 1996].

In contrast to grass and hardwood fuels, the emissions from combustion of the carbon stored in "belowground biomass" (biomass directly on top of or incorporated into the soil) are still relatively unexplored. Very high carbon loading is possible in some organic soils. For example, *Zinke et al.* [1984] report over 1000 t C per hectare in the top 1 m of North American bogs, a carbon loading about twice the maximum reported due to the aboveground biomass in tropical forests [*Brunig*, 1977]. Globally, it has been estimated that over two thirds of the carbon in forest ecosystems is contained in soils and associated peat deposits [*Dixon et al.*, 1994] and that the carbon in soils represents an even larger carbon pool than aboveground biomass [*Woodwell et al.*,

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Paper number 97JD00852.
0148-0227/97/97JD-00852$09.00

1978]. Both wildfires and land-management activities expose belowground biomass to fire, and it may account for a significant fraction of the fuel consumption in fires in the boreal forest [*Hungerford*, 1995] or in tropical forests such as the kerangas or caatinga [*Jacobs*, 1988]. It has been projected that much more of this carbon may burn in global warming scenarios [*Kasischke et al.*, 1995; *Keane et al.*, 1997]. Smoldering combustion should account for essentially all fuel consumption in burning organic soils.

In earlier work, we carried out pilot studies of the effectiveness of open-path Fourier transform infrared spectroscopy for measuring biomass fire emissions [*Griffith et al.*, 1991; *Yokelson et al.*, 1996a, b]. Our report on the laboratory pilot study [*Yokelson et al.*, 1996a] quantified the relative fire-integrated production of both reactive and stable emissions from flaming, smoldering, and pyrolysis. We followed *Ward and Radke* [1993] in using modified combustion efficiency (MCE) defined as $\Delta CO_2/(\Delta CO_2+\Delta CO)$) as an index of the relative amount of flaming and smoldering combustion occurring during a fire. We observed a correlation between emissions and MCE which independently verified the earlier work of *Lobert et al.* [1991], *Ward et al.* [1992], and others. Another major result of our pilot study [*Yokelson et al.*, 1996a, b] was observation of oxygenated volatile organic compounds (OVOC) at as much as 10 to 100 times the levels previously measured in nonspectroscopic studies. In the work of *Yokelson et al.* [1996a], we suggested that some differences between studies could be due to the different fire types probed or to the different measurement techniques employed (in particular, other studies had concentrated on hardwoods and grasses, while our measurements had been primarily on coniferous fuels). Oxygenated organic molecules, if emitted in sufficient amounts, could significantly impact plume chemistry [*Atkinson*, 1990; *Singh et al.*, 1995] and regional chemistry [*Crutzen and Andreae*, 1990]. Therefore data on the amount and type of OVOC initially produced in biomass fires will be of use in modeling the atmospheric influence of these fires.

In this paper, we address the need for information on both OVOC production and smoldering combustion of biomass by presenting some initial results from a new open-path FTIR apparatus optimized to continue the smoke measurements initiated in our pilot studies. In this work, our experimental approach was determined primarily by the following three objectives: (1) to increase the fundamental understanding of the smoldering combustion process, which may influence global climate and has other ecological effects (process level knowledge is also often useful to rationalize diverse measurement results), (2) to obtain data at several heights above fires to facilitate detecting the most reactive initial emissions and to search for evidence of rapid loss or production of species in the nascent plume, and (3) to determine whether OVOC are likely to be important emissions from most biomass fires.

Experimental Details

Fuel Selection Objectives

We burned fires in a large variety of fuels for three main reasons: (1) to investigate the natural variability in emissions from different fire types and to estimate the "boundary conditions" for initial emissions from biomass fires, (2) to increase our chance of detecting more of the species emitted from biomass fires, and (3) to enhance our ability to model the emissions from specific types of biomass fires. The fuel for each smoke sample is listed in Table 1, and the rationale for its selection in our study is summarized below.

Grass and hardwood fuels were selected because they account for a large fraction of the global biomass burning [*Crutzen and Andreae*, 1990; *Scholes et al.*, 1996] and because no in situ, spectroscopic measurements of smoke composition from fires in these fuels had been reported. Grass samples (Table 1) were rough fescue (*Festuca scabrella*, a bunch grass native to Montana) and wire grass from the southeastern United States. Hardwood fuels (Table 1) included poplar wood shavings, gallberry leaves and stems, aspen bark, and brown, partially decomposed maple leaves. The maple leaves are representative of hardwood leaf litter, a significant fuel in (temperate through tropical) seasonal, deciduous forests. We also burned one sample of banana leaves since attached leaves may comprise over one half of the aboveground biomass in some tropical secondary forests [*Uhl and Jordan*, 1984].

In some tropical pastures and secondary forests, dead wood left over from a preexisting primary forest is reported to account for a large fraction (up to 87 %) of the aboveground biomass [*Ewel et al.*, 1981, p. 820; *Uhl and Jordan*, 1984, Tables 5 and 6; *Kaufmann and Uhl*, 1990; *Barbosa and Fearnside*, 1996]. Dead wood, decomposed by either "white" or "brown" rot (fungi) [*Terron et al.*, 1995] can have percentages of cellulose and lignin very different from the 50 and 25% respectively, typically found in live wood. Brown rot removes cellulose leaving a powdery wood as high as 70 - 80 % lignin. Lignin contributes heavily to charcoal formation [*Susott et al.*, 1975; *Shafizadeh and DeGroot*, 1976] which is important in carbon cycling [*Crutzen and Andreae*, 1990], and lignin has been reported to comprise up to 48% of some peat deposits [*McMahon et al.*, 1980]. White rot preferentially removes the lignin from wood [*Terron et al.*, 1995]. For initial exploration of the effect of lignin content on biomass fire emissions, we burned one sample of Ponderosa pine wood which had been decomposed by brown rot and had a lignin content of 66.4%. Organic soil and duff samples were removed intact from various ecosystems throughout the United States (Table 1). Other fuels (Table 1) were burned mainly to increase the range of samples such as cattails and palmetto and to overlap with previous work (sagebrush).

Description of FTIR and White Cell

The IR radiation from the FTIR (MIDAC model 2500) is directed through a 1.6 m base path open White cell (Infrared Analysis, Inc.) and then refocused on an external "wideband" Mercury Cadmium Telluride (MCT) detector (Graseby FTIR M-16). (See Figure 1.) The White cell allows long path lengths to increase absorption levels (we used 70.1 or 76.5 m in all experiments reported here), and directing the IR beam through the interferometer before the long, open, atmospheric path reduces measurement noise due to emission from the hot gases [*Hanst and Hanst*, 1994]. The spectrometer was configured for a scan speed (and maximum time resolution) of 3 s at the spectral resolution of 0.5 cm^{-1} used in all measurements reported here. The spectrometer and White cell are comounted on a Super-Invar™ (Carpenter, Inc.) structure, and the mirror substrate has the lowest available thermal

Table 1. Summary of Data With Emissions Reported as 100 X (Moles Compound/Total Moles C Detected) and Moisture and Elemental Analysis Reported as a Mass Percentage of Dry Matter

		Fuel Composition				Oxides		Hydrocarbons				Aldehydes		Acids		Alcohols		Nitrogen		Sulfur
Fuel (depth, cm)[a]	Location	H_2O%	C	H	N	CO_2	CO	CH_4	C_2H_4	C_2H_2	C_3H_6	HCHO	Glycol-	Formic	Acetic	CH_3OH	C_6H_6O	NH_3	HCN	OCS
Bunch grass	Montana	88.4	37.67	5.21	1.83	87.7	9.5	0.33	0.181	0.052	0.060	0.375	0.087	0.117	0.235	0.139	0.083	0.127	0.073	0.004
Bunch grass	Montana	88.4	37.67	5.21	1.83	83.8	11.9	0.54	0.214	0.047	0.079	0.525	0.135	0.211	0.389	0.239	0.148	0.272	0.140	0.006
Wire grass	SE U.S.[b]	5.6	47.47	6.14	0.76	87.7	11.0	0.51	0.056	0.010	0.055	0.059	0.029	0.014	0.046	0.070	0.032	0.299	0.045	0.005
Poplar	SE U.S.	5.3	48.97	7.55	0.12	71.5	22.9	1.57	0.113	0.016	0.082	0.591	0.481	0.393	0.531	0.470	bld[12]	0.064	bld	0.008
Sedge[c]	Alaska	7.4	40.40	5.32	1.66	80.6	14.7	1.50	0.128	0.005	0.125	0.102	0.035	0.054	0.350	0.228	0.163	1.480	0.360	0.023
Spagnum moss[d] (0-5)	Alaska	11.1	30.02	3.76	1.28	76.9	17.1	1.07	0.180	0.014	0.171	0.307	0.107	0.159	0.630	0.274	0.259	0.312	0.222	0.007
Spagnum moss (10-25)	Alaska	11.1	30.02	3.76	1.28	82.8	13.1	1.55	0.160	0.010	0.181	0.080	0.045	0.008	0.221	0.357	0.057	1.868	0.371	0.008
Peat[e]	Minnesota	9.9	49.37	6.42	3.06	78.5	15.2	1.47	0.141	0.009	0.174	0.053	0.006	0.016	0.196	0.437	0.375	2.265	0.712	0.127
Peat[f]	Alaska	nm	nm	nm	nm	75.6	21.1	0.61	0.096	0.009	0.149	0.269	0.056	0.182	0.394	0.176	0.038	0.298	0.204	0.005
Feather moss[g] top	Alaska	17.3	45.84	6.36	0.84	81.5	15.8	0.64	0.089	0.023	0.141	0.141	0.020	0.057	0.389	0.215	0.008	0.436	0.168	0.003
Feather moss mid	Alaska	17.3	37.15	4.38	0.78	75.7	20.9	1.15	0.143	0.007	0.158	0.198	0.020	0.074	0.285	0.218	0.021	0.442	0.212	0.010
Feather moss bot	Alaska	24.0	41.01	5.34	0.93	81.8	15.7	0.78	0.087	0.012	0.090	0.084	0.016	0.043	0.250	0.224	0.015	0.712	0.228	0.005
Bog soil[h]	N. Carolina	2.6	63.95	7.82	0.70	72.2	23.9	1.50	0.179	0.012	0.155	0.073	0.014	0.063	0.231	0.226	0.068	0.063	0.298	0.021
White spruce[i] (0-5)	Alaska	13.1	38.31	4.89	1.18	82.5	13.4	1.92	0.198	0.026	0.143	0.019	0.002	bld	0.111	0.455	0.062	1.444	0.143	0.004
FF; duff[j]; pine-larch	Montana	8.9	34.25	4.72	0.95	79.5	15.8	1.62	0.165	0.007	0.147	0.111	0.023	0.043	0.343	0.533	0.107	0.900	0.231	0.009
FF; duff; pine-oak	SE U. S.	27.5	52.63	5.98	0.70	78.7	17.8	0.91	0.141	0.024	0.090	0.313	0.040	0.135	0.262	0.375	0.078	0.052	0.092	0.009
FF; duff; longleaf pine	SE U. S.	nm	50.56	6.34	1.02	65.1	26.4	1.85	0.192	0.026	0.170	0.784	0.183	0.316	0.855	1.095	0.219	0.086	0.148	0.011
Decomposed pine	Montana	34.0	52.63	5.76	0.36	76.0	19.6	1.62	0.183	0.032	0.065	0.563	0.032	0.101	0.122	0.391	0.120	0.075	0.040	0.009
Cigarette tobacco	SE U. S.	~5	42.65	4.98	3.29	88.7	6.8	1.48	0.231	0.023	0.306	0.320	0.152	0.023	0.060	0.376	0.063	2.984	0.040	0.006
Banana leaves	Indoors	5.3	41.28	5.52	2.34	79.4	15.3	0.82	0.347	0.032	0.483	0.475	0.182	0.033	0.218	0.477	0.056	2.422	0.170	0.010
Palmetto/gallberry	SE U. S.	4.9	48.50	5.83	0.63	76.6	17.1	1.20	0.104	0.008	0.103	0.161	0.029	0.002	0.850	0.428	0.339	0.476	0.103	0.009
Cottonwood bark	Montana	~5	47.91	5.10	0.45	79.5	15.2	2.21	0.211	0.013	0.128	0.201	0.044	0.035	0.345	0.567	0.108	0.522	0.018	0.009
Cattails	Montana	~5	45.40	6.14	2.58	78.6	14.8	1.69	0.315	0.012	0.336	0.234	0.132	0.159	0.600	0.438	0.146	1.680	0.151	0.020
Brown maple leaves	Montana	~5	43.19	4.47	1.34	74.9	16.9	1.99	0.275	0.040	bld	0.481	0.131	0.166	0.712	0.720	0.404	0.430	0.093	0.003
Sagebrush trunks	Montana	nm	49.53	6.14	0.67	81.0	12.6	2.43	0.151	bld	0.175	0.120	bld	0.041	0.352	0.548	0.285	0.448	bld	bld

Not measured (fuel composition measurements were omitted), nm; below detection limit, bld.

[a]The depth of soil layer sampled is provided if known.

[b]Fuels were sampled from coastal areas of Florida, Georgia, and South Carolina.

[c]Site, Tannana river valley near Tok, Alaska; fuel details, decomposing dead vegetative matter and live roots; vegetation type, subarctic wet sedge meadow.

[d]Site, Tannana river valley near Tok, Alaska; fuel details, decomposing dead vegetative matter and live biomass; vegetation type, black spruce woodland.

[e]Site, Aggasiz National Wildlife Refuge; soil order, histisol; suborder, saprist; vegetation type,sedge/grass community.

[f]Site, Tannana river valley near Tok, Alaska; fuel details, decomposing dead vegetative matter; vegetation type, peat bog.

[g]Site, Tannana river valley near Tok, Alaska; soil order, inceptisol; suborder, aquept; vegetation type, open black spruce woodland.

[h]Site, Alligator National Wildlife Refuge; soil order, histisol; suborder, saprist; vegetation type, low pocosin.

[i]Site, Tannana river valley near Tok Alaska; soil order, entisol; suborder, fluvent; vegetation type, open white spruce forest.

[j]FF; duff indicates intact cross section of forest floor with ground fuels (needles; leaves; and twigs) overlaying duff (decomposing organic matter).

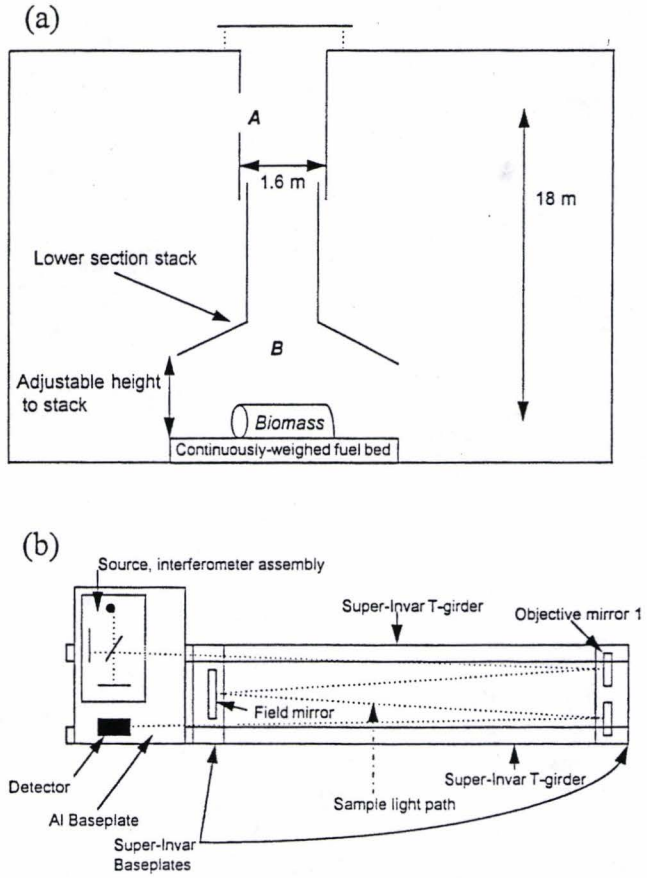

Figure 1. (a) Simplified illustration of the Intermountain Fire Sciences Laboratory combustion lab (not to scale). The Fourier transform infrared spectrometer (FTIR) was located at "A" in the pilot study and at both "A" and "B" in this study. (b) Schematic diagram of the new OP-FTIR system (not to scale).

expansion (ULE™ (ultralow expansion) Corning, Inc.). The optical throughput of the system was not measurably affected when portions of the structure were subjected to substantial, rapid increases in temperature.

Measurement Platforms and Fire Behavior

Direct measurement over low-intensity fires. Samples of organic soils listed in Table 1 (nominal size: 10 X 10 X 5 cm) were placed on Al foil several centimeters below the center of the White cell. A propane torch was used to initiate a slowly expanding "glowing pit" on the sample surfaces similar to those observed in field fires in this material [*McMahon et al.*, 1980; *Hungerford et al.*, 1995]. A very slow burning "steady state" or stable mix of glowing combustion and white smoke production (vide infra) was established within minutes. A large hood above the White cell drew the (sometimes barely visible) emissions through the optical path. The fan-induced flow was much greater than the fire-induced flow, so that the total flow was constant. Pressure and smoke temperature were also constant with smoke temperature measured to be the same as room temperature. Spectra were acquired continuously with 3 to 10 min time resolution until the size of the burning pit approached ~ 50% of the size of the sample (to prevent edge effects). The spectra of the emissions were ratioed to background spectra collected before and after the "fire" to form absorbance spectra which yielded the net concentration, above background for up to 15 compounds.

The other biomass fuels were more flammable. 15 - 900 g of sample, in a "loose" approximately "natural" configuration, were ignited with a match ~ 0.5 m below the White cell. Spectra were acquired continuously with the appropriate time resolution (3 - 120 s) throughout the period of the fire dominated by smoldering combustion. These spectra were also ratioed to background spectra collected before and after the fire. As with the soils, temperature, pressure, and flow were constant during smoldering combustion.

Single-temperature thermal analysis with enclosure. Fuels can be gently heated and produce emissions due to proximity to a fire or (in the case of soils) to increased insolation after a fire. To investigate these types of emissions, we placed samples of biomass on a hot plate (at ~ 58°C) directly below the White cell which was then enclosed on the sides and top with a sheet metal structure to slow the transport of the thermally generated substances out of the optical path. The spectra thus acquired were ratioed to background spectra acquired just before with clean air in the path.

Multitemperature thermal analysis. Biomass fuel samples were subjected to heating rates of 30° to 50°C per minute so that order of appearance for each observed product could be noted. An upper limit to the (inhomogeneous) biomass sample temperature was continuously measured at the hot plate surface. The fuel was heated just below the objective mirror end of the White cell, while the other end of the White cell was inserted about 30 cm through a window in the combustion laboratory stack. With the stack vertical flow nominally 4 m s^{-1}, the emissions (visible or otherwise) from the heated fuel were drawn horizontally through a long portion of the optical path and then up the stack within a few seconds. This optimized S:N while ensuring sufficient temporal resolution. Each fuel sample was fastened to the hot plate surface with steel wire, FTIR scanning was initiated, the hot plate was then turned to its highest setting to achieve rapid heating, and scanning continued until ignition.

Measurements 18 m above large-scale fires. A series of fires was conducted similar to those described in detail in our pilot study papers [*Yokelson et al.*, 1996a, b]. The major change was to use the new FTIR apparatus described above to acquire the spectra. In this paper, we report only results from time-averaged data acquired near the end of these fires when slow, "steady state" smoldering and little or no change in flow or temperature was observed. During one of these fires, the prefire CO_2 was measured independently by a Licor (model 6262) calibrated with National Institute of Standards and Technology traceable standards to check on the accuracy of our FTIR retrievals. (Results from the large fires have been reported elsewhere [*Yokelson et al.*, 1997].)

Auxiliary Measurements

Smoke/room temperature was measured by chromel-alumel thermocouples verified to be accurate within 0.1°C at the freezing and boiling temperature of water. Pressure (~ 90.2 kPa) was measured by the built-in pressure sensor in the Licor (model 6262). Stack flow was measured by a Kurz (model 455) mass flowmeter. Total fuel bed mass was logged every second using either one or two Mettler PM34 digital scales. Each fuel or fuel component was subsampled for

measurement of the fuel moisture and replicate measurements of the C:H:N content by a Perkin-Elmer Model 2400 CHN analyzer.

Spectrum Analysis

Two different methods were used to retrieve concentrations from spectra: (1) synthetic calibration coupled with classical least squares (CLS) fitting based on the program Multiple Atmospheric Layer Transmission (MALT) [*Griffith*, 1996] and (2) spectral integration and subtraction using commercially available software (QASOFT, Infrared Analysis, Inc. and GRAMS/386, Galactic, Inc.). In both cases, the instrument resolution is approximately equal to 3 times the width of isolated peaks due to single molecular rovibrational transitions. Under these conditions, a linear relation between concentration and absorbance holds if the analysis is restricted to features exhibiting less than ~ 0.05 peak absorbance$_{10}$ [*Anderson and Griffiths*, 1975; *Hanst and Hanst*, 1994]. This restriction can be relaxed somewhat for broadened composite features such as an entire Q branch.

MALT-CLS-based retrievals. The computer program MALT [*Griffth*, 1996] computes ideal spectra from HITRAN absorption line parameters [*Rothman et al.*, 1992], convolves these spectra with the instrument function to generate calculated spectra which closely match real experimental spectra, and generates a set of calibration spectra over a range of gas concentrations for quantitative analysis using CLS methods [*Haaland*, 1990]. MALT-CLS allows accurate analysis of any of the 32 molecules in the HITRAN database, at arbitrary temperature, without the need for acquiring reference spectra. Our usage of this method was described in detail earlier [*Yokelson et al.*, 1996a, b], and only minor changes were necessary. Because of Beer's law limitations, it was sometimes necessary to analyze spectra in newly identified regions with weaker peaks meeting the criteria noted above. In a very few cases, strong peaks of an absorber were unavoidable, and they were successfully modeled by including a "pseudocomponent" in the CLS basis set for which absorbance was proportional to the square of the concentration of the absorber [*Haaland*, 1987]. In most cases, the analysis for a compound was possible in at least two independent spectral regions. Table 2 lists all the spectral regions used to derive concentrations reported here. The concentrations in Table 1 are the weighted average of all the regions used.

Spectral-subtraction-based retrievals. For molecules for which spectral line parameters are not available, MALT-CLS cannot be used, and other methods are required. The FTIR software allows development of "custom" spectral integration/subtraction sequences using both the supplied spectral library of room-temperature reference spectra and "user" reference spectra [*Hanst et al.*, 1996]. The molecules analyzed in our sequence are listed in order in Table 2. For each molecule, an isolated feature in the smoke spectrum and integration limits, which include that peak but preclude features due to other compounds, are selected. Comparison of the integration result from the smoke spectrum and appropriate reference spectrum yields the smoke concentration for that molecule. The reference spectrum is then scaled, and its features are subtracted from the smoke spectrum to improve the analysis of the "residual" spectrum for other compounds. In a few cases, significant, unassigned residual

Table 2. Spectral Regions Used to Retrieve Concentrations Reported in This Work

MALT-CLS		Spectral Integration/Subtraction		
Compound	Spectral Region, cm^{-1}	Compound	Integration Limits, cm^{-1}	Peak, cm^{-1}
CO	2225.5 - 2217.2	H_2O	1136.2 - 1135.1	1135.7
CO	2223.4 - 2211.0	NH_3	970.0 - 960.0	967.2
CO	2056.2 - 2048.4	CH_3OH	1034.8 - 1030.0	1033.4
CO_2	2236.6 - 2223.5	HCO_2H	1106.0 - 1104.5	1105
CO_2	758.2 - 746.2	CH_3CO_2H	1185.0 1182.0	1183.8
HCO_2H	1108.9 -1100.9	C_2H_4	951.0 - 948.5	949.5
HCN	737.0 - 724.7	C_3H_6	912.9 - 911.8	912.4
HCN	734.4 - 722.8	$C_2H_4O_2$	1115.4 - 1113.5	1114.6
HCN	717.1 - 708.8	$C_2H_4O_2$	861.4 - 857.0	860.4
HCN	3352.6 - 3338.7			
HCN	3324.3 - 3316.1			
HCN	3253.2 - 3246.9			
NH_3	818.4 - 801.3			
NH_3	837.0 - 829.6			
NH_3	969.8 - 956.8			
CH_4	1309.9 - 1291.5			
CH_4	3020.5 - 3006.5			
H_2CO	2771.1 - 2763.2			
H_2CO	2783.8 - 2776.3			
H_2CO	2888.5 - 2879.3			
H_2CO	2901.2 - 2890.0			
C_2H_2	737.0 - 724.7			
C_2H_2	734.4 - 722.8			
OCS	2092.7 - 2028.8			

Unknowns remain at 2848, 853, and 805 cm^{-1}.

absorption remained after the subtractions of the sequence were performed. The peak wavelengths of features which are still unassigned are listed in Table 2.

With the exception of 2-hydroxyethanal, the reference spectra used in our sequence were derived by reducing the resolution of the supplied high-resolution (0.125 cm^{-1}) spectra in the Fourier domain to match the resolution of our experimental data. We obtained a relative 2-hydroxyethanal cross section by warming crystals on a hot plate below the multipass cell and put this relative cross section on an absolute scale by comparison to a resolution independent part of the absolute 2-hydroxyethanal spectrum published by *Niki et al.* [1981].

Accuracy and Detection Limits

The nominal accuracy of both the molecular line parameters in HITRAN and the commercially supplied reference spectra is 5% or better [*Rothman et al.*, 1992; *Hanst and Hanst*, 1994]. The precision and accuracy of our MALT-CLS data are indicated by plotting against each other the concentrations retrieved for the same molecule in the same spectrum but from different spectral regions. Typical comparisons (see Figure 2) yield a slope and *r*-squared value of 0.985 and 0.98 for CH_4 and 1.007 and 0.99 for CO_2. NH_3 and formic acid were analyzed by both methods. We plotted the results from the MALT-CLS approach versus the results from the spectral subtraction protocol and obtained agreement at the 10% level which we deemed sufficient at this time. Finally, we compared the concentration of CO_2 derived from MALT-CLS analysis of a single-beam spectrum of background air to that obtained by simultaneous measurement with a nondispersive infrared CO_2 analyzer (Licor Model 6262). The MALT-CLS retrievals from the two independent spectral regions used had a weighted average of 378 ppm. The Licor simultaneously indicated a concentration of 384 ppm which is about 1.5% higher. On the basis of the above results, the uncertainty in the individual concentration measurements is $\leq$ 10 % (1σ) or the detection limit, whichever is greater. The detection limits are different for each species and for each spectrum but are normally in the low "tens" part per billion (ppb) when > 70 m path lengths are used.

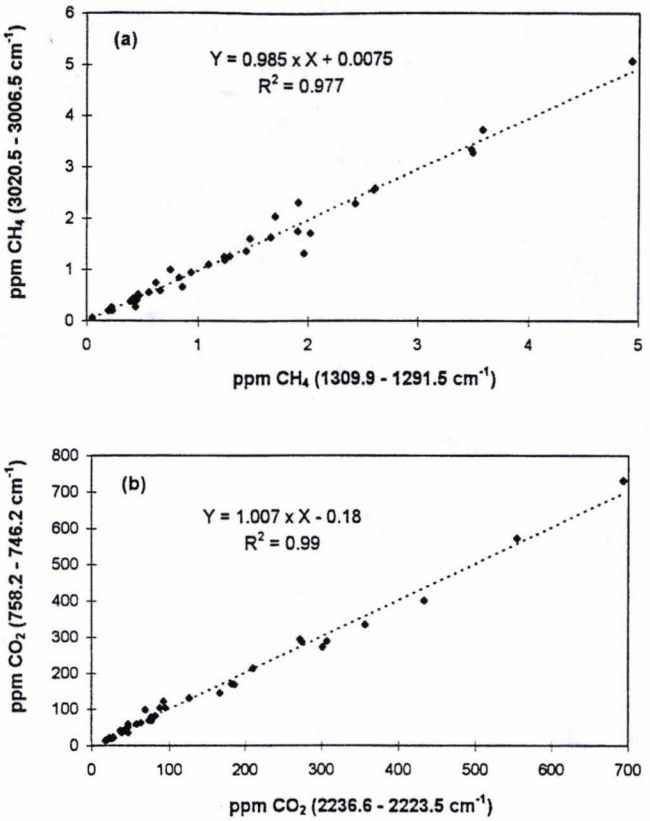

Figure 2. In each plot the concentrations derived from Multiple Atmospheric Layer Transmission-classical least squares analysis of two independent regions of the same spectra are plotted versus each other (see text). (a) Concentrations from ν_3 versus ν_4 for CH_4. (b) Results from ν_2 versus ν_3 for CO_2.

Results and Discussion

Scope of Results

We have investigated 24 small fires and, in the process, collected over 1000 individual real-time spectra. Since temperature, pressure, and flow were all constant during smoldering in these fires, the mixing ratios from the spectra acquired during the time dominated by smoldering combustion have been averaged together for each of the 24 fires in Table 1. For each fire listed in Table 1, the fuel, fuel sample location, fuel moisture, and fuel C:H:N content are indicated as well as the emissions detected. (The C:H:N analysis is listed for the bulk material, and the soils contained from 2 - 60% inorganic material.) Fifteen molecules were normally present in the smoke at concentrations well above the detection limits including carbon dioxide, carbon monoxide, methane, ethene (C_2H_4), ethyne (C_2H_2), propene (C_3H_6), formaldehyde (H_2CO), 2-hydroxyethanal ($CHOCH_2OH$), methanol (CH_3OH), phenol (C_6H_5OH), acetic acid (CH_3COOH), formic acid (HCOOH), ammonia, hydrogen cyanide (HCN), and carbonyl sulfide (OCS). This list excludes water and four other molecules which were measured in our pilot study [*Yokelson et al.*, 1996a]. Three of these molecules (NO, NO_2, and SO_2) are readily detectable with our apparatus but are formed primarily by flaming combustion [*Yokelson et al.*, 1996a]. A number of spectra were checked for evidence of these compounds. None showed evidence of NO and only one contained evidence of NO_2 and SO_2 (near the current detection limits of about 20 ppb). Ethane (C_2H_6) was readily detected in the current spectra of emissions from "pure" glowing combustion at an average molar ratio to methane of 7.4% in excellent agreement with average values of this ratio reported by *Lobert et al.* [1991] (7.5 %) and *Hao et al.* [1996] (7.4%). However, since C_2H_6 was near, or below, our detection limits in the majority of the spectra, the data are not included in Table 1.

Fire Behavior and Emissions-Producing Combustion Processes

Visual observation of an initial series of fires provided a framework for our subsequent spectroscopic observations. The fuel for these fires was (~ 30 X 30 X 10 cm, average mass ~ 1 kg) pine needles, wooden sticks, or hardwood shavings and was ignited with a match. Black smoke was generated just above the flame tips. White smoke was generated (initially) by

heating of the fresh fuel adjacent to the flame front. Glowing combustion began on the fuel elements before flaming ceased. After flames ceased, glowing combustion continued and generated white smoke by heating that part of the fuel element which was not yet glowing. For thin fuels ($\leq \sim 1$ mm), glowing soon covered the whole fuel element and then continued for some time alone, producing emissions but not visible smoke. Thus, in thin fuels, white smoke appeared as an accompaniment to flaming and as an interlude after flaming. For larger fuel elements (such as plant branches or organic soils), glowing and white smoke production coexisted long after any flaming. Placing fresh biomass on top of glowing combustion or a hot plate caused production of white smoke which could be readily ignited to initiate flaming. Alternatively, continued heating of the fresh biomass also often culminates in ignition of the white smoke.

Spectra of Emissions From Specific Thermal and Combustion Processes

The black smoke, white smoke, and glowing emissions were found to contain very different products. Figure 3 shows the same spectral region (the "fingerprint" region) from two different spectra acquired at different times during the same fire in thin hardwood fuel. The top spectrum is of the fire products when white smoke and glowing combustion coexist just after the cessation of flames. The bottom trace was acquired ~ 50 s later, when only glowing combustion, with no visible smoke production, was observed. As indicated in figure 3, the top ("white smoke plus glowing") trace is dominated by the features of acetic acid, formic acid, methanol, ethene, and 2-hydroxyethanal but also includes smaller features due to NH_3 and CH_4. In contrast, the "fingerprint" spectrum of the glowing emissions is remarkably simple and consists almost entirely of NH_3 and CH_4 features. Similarly, in the "C-H stretch" region (2700 - 3100 cm^{-1}), H_2CO and heavy NMHC's were observed only in the "white smoke plus glowing" spectrum. In the "smokeless glowing" spectrum, the C-H stretch region only shows strong features due to CH_4 and weak features due to C_2H_6.

We conducted "temperature ramp" experiments (as described in the experimental section) to isolate the pyrolysis process and determine whether "pure white smoke" contains NH_3 and CH_4. For both pine needles and hardwood shavings, white smoke generation preceded the onset of glowing as the fuel temperature was increased. In the spectrum of white smoke acquired before glowing combustion was present, the sharp features were due only to H_2O, H_2CO, CH_3OH, CH_3COOH, and HCOOH. Methanol had the lowest "appearance temperature" from pine needles, perhaps because (in addition to being a pyrolysis product) it is a significant biogenic emission [*MacDonald and Fall*, 1993; *Konig et al.*, 1995]. Ammonia and methane were observed only in the spectra acquired at higher temperatures when visible glowing combustion had begun. In a related, fixed-temperature experiment, heating green pine needles (at 58°C) produced high levels of β-pinene. In all the "white smoke plus glowing" spectra, or the spectra acquired early during temperature ramps, the shape of the "C-H stretch region" also resembles monoterpene spectra. The thermal order in which these compounds are observed is in good agreement with numerous other works [*Lephardt and Fenner*, 1980; *Evans et al.*, 1986; *DeGroot et al.*, 1988; *Jakab et al.*, 1993]. In summary, initial heating of fresh fuel produces a flammable mixture of oxygenated compounds and unsaturated hydrocarbons, subsequently, alkanes and NH_3 are produced at higher temperatures, apparently in conjunction with visible glowing combustion.

Summary of Emission Production Chemistry

The black smoke associated with flaming consists primarily of CO_2 and other highly oxidized compounds

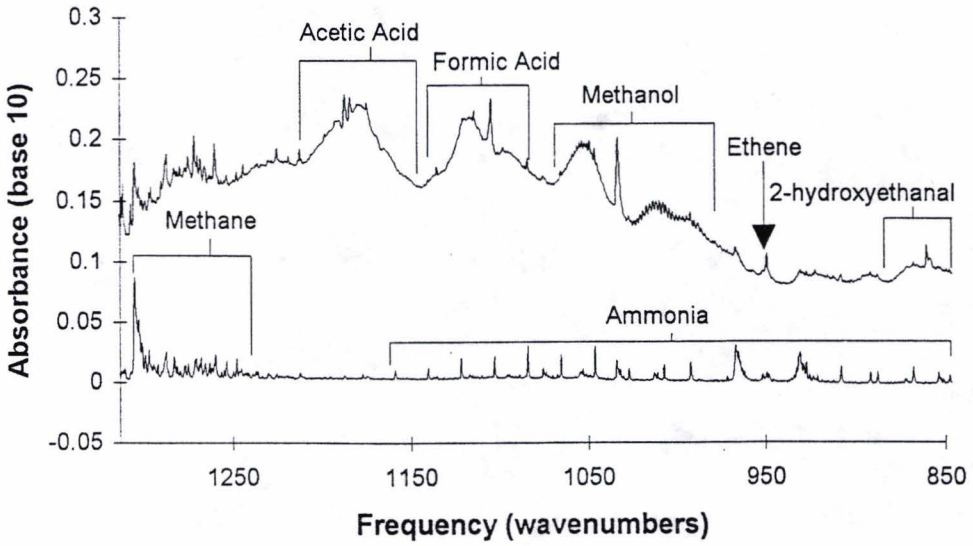

Figure 3. The top trace shows the "fingerprint region" of a smoke spectrum from a fire in thin hardwood fuel elements that is producing white smoke at the same time that glowing combustion is observed. The bottom trace is the same spectral region for the same fire ~ 1 min later when white smoke production has ceased and only glowing combustion is observed. The top (white smoke plus glowing) trace is dominated by strong features due to the indicated oxygenated organic compounds. The lower (glowing only) trace shows features due to CH_4 and NH_3 only. (CO_2 and CO features are present in both traces in a spectral region not shown here.)

[*Lobert et al.*, 1991; *Ward and Radke*, 1993; *Yokelson et al.*, 1996a] as well as carbonaceous aerosol [*Radke et al.*, 1991]. In contrast, the white smoke produced by heating fresh fuel is rich in pyrolysis or "distillation" products (such as formaldehyde, 2-hydroxyethanal, methanol, phenol, and organic acids) and (probably) "heavy hydrocarbons." Glowing combustion, in the absence of visible flames or smoke, did not produce oxygenated compounds or "heavy hydrocarbons" but did produce a good deal of excess CO_2, CO, CH_4, and NH_3. The CO_2 and CO (the major emissions of "smoldering combustion") probably arise predominantly from gassification of char which includes the following reactions [*Hshieh and Richards*, 1989; *Kannan and Richards*; 1990].

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad (1)$$

$$C_{(s)} + CO_{2\,(g)} \rightarrow 2CO_{(g)} \quad (2)$$

CH_4 and NH_3 may arise from simultaneously occurring aromatization of low temperature char [*Yokelson et al.*, 1996a, Figure 7]. Another possible source of CH_4 and CO could be the following reaction which is more thermodynamically favored than the well known "water-gas reaction."

$$C_{(s)} + CH_3OH_{(g)} \rightarrow CH_{4(g)} + CO_{(g)} \quad (3)$$

The model fire emissions were due to a combination of at least three very different, temporally overlapped combustion processes. Each process produces its own mix of emissions (including some reactive gases), and the relative weighting of these processes can sometimes change rapidly leading to a rapid change in smoke composition. These observations are consistent with at least one airborne fire observation where the albedo of smoke was determined to be higher for smoldering combustion [*Radke et al.*, 1991]. The dynamics observed in the model fires should be considered in the design of field emissions-measurement programs and microscale plume models. The process-level knowledge developed here may have some predictive power for assessing field fire impacts on the atmosphere. For instance, deforestation fires which feature large fuel elements and a high percentage of fuel consumption by "smoldering" [*Susott et al.*, 1991; *Ward et al.*, 1992] might be predicted to inject especially large quantities of oxygenated organics into the atmosphere. It is also possible that photographs of field fires may assist in qualitatively estimating their emissions.

Production of Oxygenated Compounds

Open-path FTIR measurements of smoke composition from hardwood, grasses, and other fuels. In *Yokelson et al.* [1996a], we thoroughly compared our open-path FTIR measurements of OVOC with other published measurements for which there were sufficient auxiliary data to compute a modified combustion efficiency (MCE). We noted that, compared to other nonspectroscopic studies, our study showed much higher production levels and a strong correlation with MCE which was absent from other work. We speculated that a possible cause of this inconsistency was a difference in the fuels burned. In particular, most of the other studies featured hardwood or grass fuels as opposed to the mainly coniferous fuels used in our pilot study. In part, that hypothesis was supported by the fact that acetic acid and methanol were below our detection limit when sagebrush was burned in the pilot study. However, both these compounds are clearly produced in the sagebrush fire in this work which featured white smoke production and glowing combustion coexisting on the trunks for a prolonged period after the cessation of flaming. The ratio of methanol or acetic acid to CO produced in our current sagebrush fire would have been observable in the pilot study sagebrush fire had it occurred.

Figure 4 shows the data for acetic acid, methanol, and formaldehyde from mostly coniferous fuels, which were compared with other work by *Yokelson et al.* [1996a], coplotted with data for the same molecules from the grass fires in our current work. The data from the pilot study are fire-integrated and from fires featuring both flaming and smoldering, while the data from the current work represent a series of "snapshots" of smoldering combustion only. The linear response function for OVOC production versus MCE is different for the two fuel/fire types, but a single line can be fit reasonably well to the combined data sets, and that is shown here to indicate the qualitative consistency between our two measurement sets separately obtained from grass and coniferous fuels which is in contrast to the very large differences between studies shown by *Yokelson et al.* [1996a].

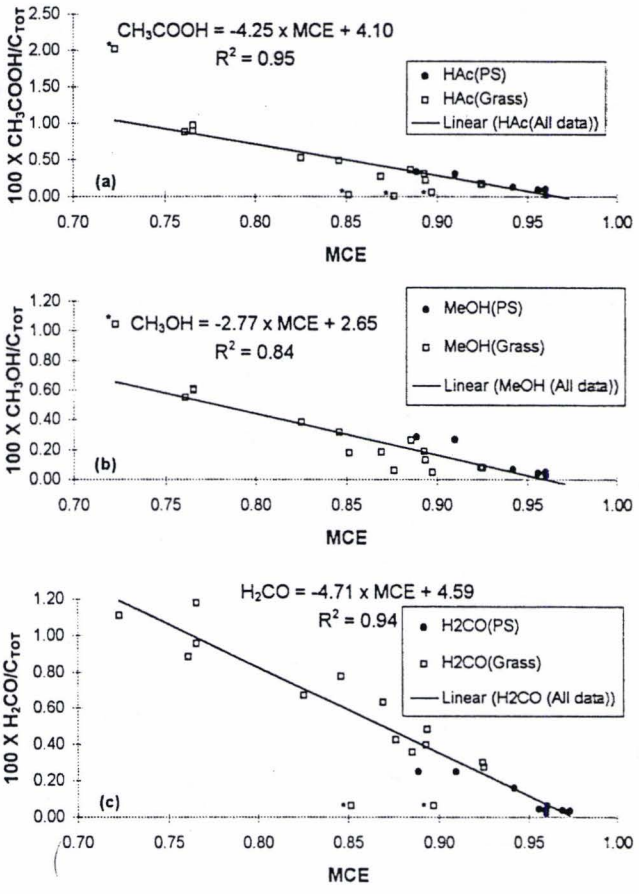

Figure 4. The real-time production for (a) formaldehyde, (b) acetic acid, and (c) methanol, versus modified combustion efficiency from grass fires in this work, is coplotted with the fire-integrated measurements for the same compounds, but in mostly coniferous fuels, reported by *Yokelson et al.* [1996a]. The *y* axis quantity is the mole percent of compound relative to total carbon emitted and detected. Points treated as outliers and not included in the indicated fit are marked with an asterik.

The above observations suggest that the large differences between studies discussed by *Yokelson et al.* [1996a] are mainly due to differences in fire behavior or measurement technique [*Cofer et al.*, 1985; *McKenzie et al.*, 1995] rather than a difference in fuels. In particular, there are differences in experimental design between our work and that of *McKenzie et al.* [1995] which may limit the validity of detailed comparison.

Real-time OVOC production was both substantial and well correlated with real-time MCE for the "duff" fuels burned in this work. Real-time data for OVOC production from hardwood fuel was less correlated with real-time MCE, but (Table 1) OVOC accounted for more than 2.5 % of the carbon produced. Only a few correlations stand out in the data from the diverse organic soils burned in this work, but OVOC do account for ~ 0.5 to 2.0 % of the carbon production which is qualitatively similar to the amount observed for methane. Taken together, these observations suggest that OVOC production in most real fires is likely to be significant.

Observation of 2-hydroxyethanal. Prominent narrow absorption features due to 2-hydroxyethanal (hydroxy-acetaldehyde and glycolaldehyde) appear in all the spectra of white smoke. Table 1 shows that this compound, previously unreported in smoke, is a significant emission from biomass fires accounting for up to ~ 1% of the carbon detected in the emissions. Figure 5 shows that 2-hydroxyethanal production is about one third of formaldehyde production during smoldering combustion in our bunch grass fires. The 2-hydroxyethanal features also account for the largest (formerly) unassigned peaks in the pilot study spectra, some of which were reanalyzed to yield 2-hydroxyethanal at ~ one fourth the formaldehyde production, in reasonable agreement with the present data set. Observation of this compound is not surprising as 2-hydroxyethanal is usually the dominant product that arises from fast pyrolysis of untreated cellulose [*Richards*, 1987; *Radlien et al.*, 1991].

Little is known about the atmospheric chemistry of 2-hydroxyethanal. The Henry's law constant [*Betterton*, 1992] limits its atmospheric lifetime to 3 - 5 days. However, aldehydes are expected to react with HO_2, OH, and tropospheric solar radiation on the timescale of hours [*Finlayson-Pitts and Pitts* 1986, Figure 3.45 and page 507]. Secondary production of this compound in smoke plumes is also likely to be significant. *Niki et al.* [1981] measured a 20% yield of 2-hydroxyethanal from the reaction of OH and C_2H_4 in the presence of NO_x, and the atmospheric modeling studies of *Calvert and Madronich* [1987] found α-hydroxy-carbonyls to be a significant product channel in the oxidation of alkenes. Our data indicate that 2-hydroxyethanal and C_2H_4 are initially emitted in comparable amounts, and thus the direct emission of 2-hydroxyethanal may dominate the secondary production in the early plume. In modeling air pollution due to fossil fuel combustion, OVOC are important as secondary photochemical products; however, in the combustion of biomass (~ 45 % oxygen), OVOC are also important as initial products.

Lignin content and OVOC production. Lignin is a polymer composed of phenol-like subunits and has lower oxygen content than cellulose [*Evans et al.*, 1986]. High lignin content would be expected to correlate with lower OVOC production and higher emissions of phenol-like compounds. Lignin content was only measured for the decomposed pine (66.4 %). The only phenol-like compound we detected was phenol itself. A preliminary, qualitative comparison can be made between the undecomposed poplar sample (which is high in cellulose content) and the decomposed pine. Table 1 shows that poplar smoke contains about twice the ratio of (total OVOC)/(total C) as smoke from the decomposed pine. The 2-hydroxyethanal and organic acids are clearly lower from the "rotted" wood, and phenol is clearly lower from the poplar. Methanol and formaldehyde are prominent in both samples. Phenol is also produced in large amounts from decomposed maple leaves and other samples. This could be due to lignin and/or the presence of other phenolic compounds which can occur in significant quantities in leaves, litter, or soils [*Jacobs*, 1988; *Flaig*, 1971]. More study is needed to determine if lignin content is a useful predictor of emissions. Phenol was also reported, but as a comparatively minor product, in the study of *McKenzie et al.* [1995].

According to *Atkinson* [1990], phenol is produced in the atmosphere by oxidation of benzene. Our average phenol/CO is 0.69 % which is about 3 times the benzene/CO ratio of 0.21 % reported by *Lobert et al.* [1991]. Again, this illustrates the

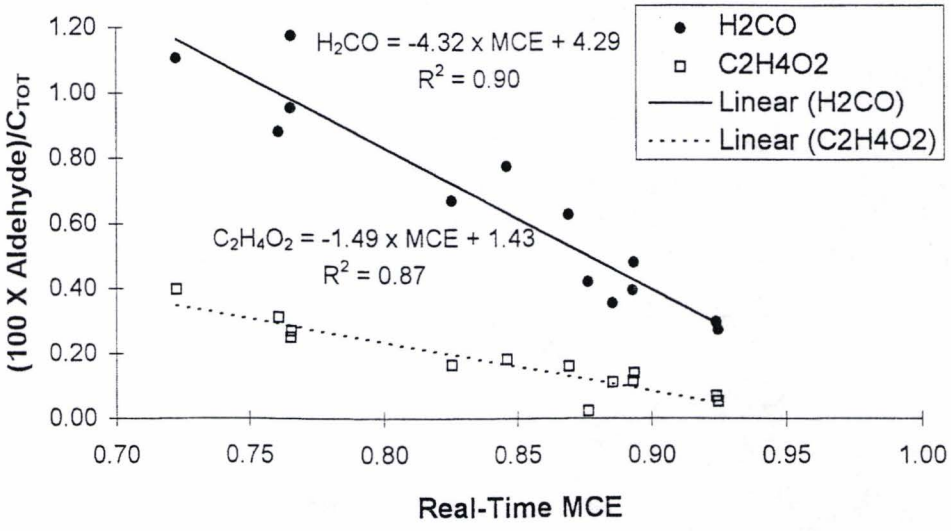

Figure 5. Real-time formaldehyde and 2-hydroxyethanal production from bunch grass fires is plotted versus real-time modified combustion efficiency.

high relative importance of initial emissions of oxygenated compounds from biomass combustion. Phenol would react quickly with NO_3 at night to yield nitric acid while reaction with OH during the day evidently yields pyruvic acid, then acetaldehyde [*Atkinson*, 1990], and eventually (primarily) methyl radicals through reaction with OH [*Finalyson-Pitts and Pitts*, 1986]. In a related note, phenolic compounds, attributed to lignin pyrolysis and extracted from particulate, have been investigated extensively as tracers for biomass combustion [*Simoneit et al.*, 1993, and references therein].

Production of Nitrogen and Sulfur Compounds

In the work of *Yokelson et al.* [1996a], we noted that the bulk of available evidence indicated that HCN was relatively unimportant in accounting for fate of fuel nitrogen and that NH_3 was the dominant, detected, nitrogen-containing product of smoldering combustion. Most of our current results with aboveground biomass (Table 1) also support that conclusion. However, with organic soils included, the HCN/NH_3 ratio varies about 2 orders of magnitude. For the fire in the sample of North Carolina bog soil, HCN production actually dominated ammonia production by a factor of 5. The chemical makeup of organic soils has been reviewed by *Flaig* [1971]. In most cases, over half of the nitrogen is contained in amino acids [*Flaig*, 1971; *Sowden et al.*, 1978; *Gonzalez-Prieto and Carballas*, 1991] which are "artifacts" formed during analysis by acid hydrolysis of plant or microbe proteins. The high-temperature pyrolysis of some amino acids has been shown to yield NH_3 [*Djilas et al.*, 1994], but others may preferentially pyrolyze to yield HCN. Alternately, steam distillation of soil nitrates is a source of NH_3 [*Stevenson*, 1982], and consistent with this, there was a tendency for the drier soils to produce a higher HCN/NH_3 ratio. A systematic study of this second effect is both feasible and warranted. In summary, the high N content of the organic soils, combined with the lack of flaming combustion, caused very large emissions of NH_3 (as much as 16% of CO and 3 % of CO_2), considerable HCN emissions, and insignificant NO_x emissions. The spectra of smoke from the soil sample highest in N did not yield evidence of any of the 32 other nitrogen-containing compounds for which we have reference spectra (including HNO_3). These facts should be considered in assessing the impact of fires in the boreal forest. Tropical vegetation has a higher tendency than temperate vegetation to store nutrients in the leaves [*Jordan*, 1985], and levels of NH_3, as high as in soil fire emissions, were also produced from the smoldering banana leaves. However, unlike the organic soils, the banana leaves were primarily consumed by flaming combustion.

The N:C ratio (defined as (NH_3 + HCN)/C_{tot}) detected in the emissions from smoldering soils was about one half the N:C ratio in the biomass. This reflects our inability to detect N_2 [*Kuhlbusch et al.*, 1991; *Yokelson et al.*, 1996a] and the presence of inorganic nitrogen which would "inflate" the biomass N:C ratio. The N balance is also affected by tar formation. The tar yield was measured twice at slightly over 1% by mass; however, the tar was enriched in N by a factor of 6 to 7 over the parent material. (Gentle heating of the tar produced NH_3 as well as acetic acid and heavy hydrocarbons.)

The only sulfur compound we report is carbonyl sulfide, and biomass sulfur content was not measured. OCS emissions correlated with soil nitrogen contents (r^2 = 0.87) suggesting that sulfur and nitrogen content are correlated in our soil samples. There was evidence of small amounts of SO_2 from the peat sample with the highest nitrogen content, but we did not quantify SO_2 as we have shown earlier that it is primarily produced by flaming combustion [*Yokelson et al.*, 1996a].

Estimates of Initial Emissions for Atmospheric Models

The results presented here and by *Yokelson et al.* [1996a] show clearly that different fire types may emit compounds in quite different relative proportions. In addition, the initial emissions will vary throughout a single fire [*Lobert et al.*, 1991; *Yokelson et al.*, 1996a, Figures 4 - 6], and (except for CO_2 and CH_4) most of the dominant biomass fire emissions are too reactive to be well mixed in the global troposphere [*Prather et al.*, 1994]. Therefore the influence of individual fires could vary strongly depending on the fire type and the state of the atmosphere. We plan detailed, microscale modeling of fire plumes to investigate these and other effects. Regional models (including transport) have demonstrated important links between fire emissions and regional tropospheric chemistry as noted earlier. These studies model the transformation of the emissions resulting from many fires burning simultaneously in a source region, and therefore a reasonable estimate of the initial emissions from an "average" fire in the source region is of use. The initial fire emissions for a number of atmospherically significant compounds have now been measured by OP-FTIR, and these data are presented in Table 3 with each species reported simply as a ratio to CO or CO_2 (for reasons discussed below). (In Table 3 an "average" appropriate for the more commonly modeled tropical scenarios is derived from the current data by weighting the average of the three grass fires equal to the hardwood fire and the average of all the other fires.) The spectroscopic data in Table 3 should be combined with data from other sources such as gas chromotography (GC)/flame ionization detection data for hydrocarbons, GC/electron capture detection data for halogenated organics, the H_2 data of *Cofer et al.* [1988, 1990], and field data for CO and CO_2 from fire types of interest for a more complete characterization of the initial emissions.

We use several different emissions reporting methods in this work for reasons explained next. Plotting emission factors versus MCE can represent well how emissions vary with fuel type or fire combustion characteristics and facilitate the intercomparison of data sets. The plot of emission factors versus MCE for smoldering and pyrolysis compounds is often well fit by a line which has a negative slope and passes nearly through the x intercept of 1. This is approximately algebraically equivalent to the assumption that the compound is emitted in a constant ratio to CO, independent of MCE. Thus we use the compact "ratio" format in Table 3 with reasonable accuracy for estimating the initial emissions of an "average" regional fire. However, it is important that pyrolysis compounds do not track temporally with CO which implies serious limitations in the representativeness of grab sampling [*Yokelson et al.*, 1996a]. Fire-integrated emissions of pyrolysis compounds do scale reasonably well with fire-integrated CO. In the work of *Yokelson et al.* [1996a], the ratios of pyrolysis compounds to CO measured during smoldering were only (on average) 60% of the same ratio determined over the whole fire. With this in mind, the entries in Table 3 from this work for pyrolysis compounds may be a

Table 3. A Summary of in Situ, Spectroscopic, Biomass Fire Emission Measurements Expressed as Percentages of CO_2 and CO

Study	Emissions as Percent of CO_2		
	NO	SO_2	NO_2
Griffith et al. [1991]	0.095	nm	0.050
Yokelson et al. [1996a]	0.178	0.063	0.050

	Emissions as Percent of CO													
	Hydrocarbons					Aldehydes		Acids		Alcohols		Nitrogen[a]		Sulfur
	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	HCHO	Glycol-	Formic	Acetic	CH_3OH	C_6H_6O	NH_3	HCN	OCS
Griffith et al. [1991]	7.61	nm	nm	nm	nm	1.27	nm	nm	nm	nm	nm	3.24	0.12	nm
Yokelson et al. [1996a]	10.86	1.42	1.71	0.98	nm	1.60	nm	0.73	2.32	1.61	nm	1.91	0.44	nm
This work	6.55	0.45	0.98	0.17	0.65	2.33	1.08	1.09	2.20	1.98	0.84	2.66	0.65	0.04
Average all	8.34	0.94	1.35	0.57	0.65	1.73	1.08	0.91	2.26	1.80	0.84	2.60	0.40	0.04

Not measured, nm.

[a]If fuel N data are available, Figure 12 and text of *Yokelson et al*. [1996a] can be consulted to partition NH_3 and NO_x.

lower limit. In summary, the data presented in this paper and *Yokelson et al.* [1996a, b; 1997] suggest that it is desirable to include OVOC as important initial constituents in regional atmospheric chemistry models of biomass burning plumes. All spectroscopic work is consistent with the following summary of fire-integrated emissions. CO_2, CO, and CH_4 are the three dominant emissions and a fourth "tier" (just below methane) includes methanol, acetic acid, formaldehyde, ethene, ammonia and nitric oxide.

Preliminary Search for Evidence of Chemical Reactions in the Smoke Plume

A careful search of our spectra reveals no features due to a number of reported smoke compounds such as nitric acid [*Lobert et al.*, 1991] or acetone [*Singh et al.*, 1994] which should have been well above our detection limits if initially produced at the levels reported by other workers. One possible explanation for this is rapid secondary generation of chemicals in the plume. For instance, the reaction of OH with NO_2 or the reaction of NO_3 with C_6H_6O could form HNO_3. It has been suggested that acetone could form from oxidation of fire-volatilized terpenes [*Singh et al.*, 1994; *Arnts and Gay*, 1979; *Gu et al.*, 1984]. In principle, comparison of our data from several centimeters and 18 m above fires could yield some evidence of the earliest 3 - 5 s of chemical transformations. However, initial inspection of our data shows no gross differences between data collected at the different elevations (i.e., there are no compounds which appear only at one elevation). Laboratory determination of these effects will require additional experiments and a light source capable of driving photochemistry.

Conclusions

The high temporal resolution and broad sensitivity of open-path FTIR has contributed to better understanding of combustion-process effects on biomass fire emissions. For example, we demonstrate that white smoke generated by fuel pyrolysis is the major source of oxygenated organic molecules. The production levels of oxygenated organic compounds observed in our earlier work [*Yokelson et al.*, 1996a] were high compared to other work at the time, but these levels have been verified by the current measurements, directly above a wide variety of biomass fires. The compound 2-hydroxyethanal was discovered to be a significant fire emission. On the basis of its role as an initial biomass fire emission and probable secondary gas-phase product, we suggest that the atmospheric chemistry of 2-hydroxyethanal warrants further investigation. Suggestions for incorporating oxygenated organic compounds into plume models are given. We have verified the well-recognized dependence of fire emissions on combustion efficiency [*Ward and Radke*, 1993] and on fuel which should be factored (as possible) into assessments of fire impacts on the atmosphere. For instance, the ratio of NH_3/HCN can range from greater than 10 to as little as one fifth depending on the fuel and combustion conditions.

Acknowledgments. The authors would like to thank Geoff Richards of the Shafizadeh Center for Wood and Carbohydrate Chemistry, University of Montana, for informative discussions and Roger Petterson of the USDA Forest Products Laboratory for providing a lignin analysis. This research was supported by a USDA, Forest Service, Research Joint Venture Agreement USFS RJVA95009 and by the National Science Foundation under grant ATM-9631219.

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Received October 11, 1996; revised March 10, 1997;
accepted March 10, 1997.

Spectroscopic Studies of Biomass Fire Emissions

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Abstract. Biomass from a diverse range of ecosystems including: coniferous forests, hardwood forests, grasslands, and organic soils was burned both in the field and in the Intermountain Fire Sciences Laboratory open combustion facility. Mid-infrared spectra of the nascent emissions were acquired at several heights above the fires with a Fourier transform infrared spectrometer (FTIR) coupled to an open multipass cell or a telescope and a remote IR source. Open-path FTIR (OP-FTIR) is capable of measuring a wide variety of reactive and stable gases with high (seconds) time resolution and these are the first applications of this technique to determine the trace gases in smoke from biomass fires. The products detected are classified by the type of process that dominates in producing them. From flaming combustion we measure carbon dioxide, nitric oxide, nitrogen dioxide, sulfur dioxide, and water vapor. From smoldering combustion we measure carbon dioxide, carbon monoxide, methane, ammonia, and ethane. About one-half of the detected organic emissions arose from fuel pyrolysis which produces white smoke rich in oxygenated organic compounds; examples are methanol, phenol, formaldehyde, hydroxyacetaldehyde, acetic and formic acid, ethene, ethyne, propene, carbonyl sulfide, and hydrogen cyanide. These pyrolysis compounds are likely to have a more important role in plume chemistry than previously thought. Our work suggests that, normally, nearly all the fuel nitrogen can be accounted for by measuring NO_x, NH_3, ash N, and N_2. While NH_3 is normally the major nitrogen-containing emission detected from smoldering combustion of aboveground biomass, from some smoldering organic soils HCN was dominant. Tar condensed on cool surfaces below all the fires accounting for ~ 1 % of the biomass burned, but it was enriched in N by a factor of 6 - 7 over the parent material and its possible role in post-fire nutrient cycling should be further investigated. The large differences and rapid changes in emissions from different fire and fuel types demonstrate that OP-FTIR is emerging as an indispensable technique for biomass fire emissions characterization.

Introduction

Biomass burning is an important land management tool [*Goldammer and Penafiel*, 1990] and energy source [*Brink et al.*, 1976]. However, biomass burning also injects significant amounts of trace gases and particles into the global atmosphere [*Crutzen and Andreae*, 1990; *Crutzen and Carmicheal*, 1993; *Prather et. al.*, 1994; *Prather and Logan*, 1994] and can profoundly effect regional atmospheres. The major fire emissions and their probable atmospheric effects have been reviewed [*Crutzen and Andreae*, 1990]. The major effects of the trace gases are summarized here. Fires may cause up to 20% of the recent increase in greenhouse gases primarily by emitting CO_2 and CH_4. CO and CH_4 consume OH radicals which clean the atmosphere. Oxygenated organic compounds can be pollutants and contribute to acid precipitation, but are also precursors for the formation of OH. NO and NO_2 are pollutants, contribute to the acidity of precipitation, and in the presence of hydrocarbons photochemically form tropospheric O_3 (which is itself a greenhouse gas and a pollutant). Halogenated hydrocarbons may affect the concentration of stratospheric O_3.

Quantification of representative emissions from fires is difficult, and different configurations of analysis techniques and sampling platforms have been utilized. Aircraft can probe a large area of emissions, investigate secondary chemistry, and provide details on transport [*Andreae et al.*, 1988]. The transport/dilution details are crucial as the rate of chemical transformations is often proportional to the product of the precursor concentrations and the photochemistry of many species is strongly dependent on altitude [*Chatfield et al.*, 1996]. However airborne sampling is expensive, it is difficult to monitor a single fire continuously from beginning to end, and it is difficult to correlate measurements with knowledge of the specific fuels and fire types. Ground-based measurements provide the opportunity for more detail on the fire and fuels [*Delmas et al.*, 1991], but may tend to incorrectly estimate the emissions in the convection column above the fire [*Andreae et al.*, 1988]. Tower-based, simultaneous measurements of concentrations and flow have been implemented as a means of more representative ground-based sampling [*Ward et al.*, 1992].

Despite the importance of field measurements, there are also a number of advantages to studying modeled biomass fires in the laboratory including:

1. All the smoke is captured from a whole fire and a good cross-section of it is probed at all times. This is not achievable in the field and that introduces uncertainty in field results.
2. Simultaneous measurements of flow, temperature, and mass-loss as well as smoke composition by redundant instrumentation are relatively easy to carry out. This facilitates rigorous intercomparisons and leads to better accuracy estimates. More complete knowledge of the chemical and physical characteristics of the fuel bed is possible.
3. The smoke is most concentrated directly above fires which offers the opportunity to detect the most species.
4. The IFSL facility, in particular, is the large enough to simulate many types of wildland fuel combustion on a realistic scale (e.g. > 3 m flame lengths are possible if desired).

In addition to the challenges presented by the need to sample fires representatively, there is the additional challenge of identifying instrumental techniques that can cope with hot, reactive samples where the potential for chemical interference and the dynamic range of concentrations is very high. Many smoke composition measurements have been made but, until recently, only with a limited suite of instrumentation. This increases the uncertainty in smoke composition due to omissions or errors resulting from the inherent limitations of the sampling methods employed and limits the accuracy of models of the effects of fire on the atmosphere. The advantages of an in-situ, open-path FTIR-based study of biomass fires include:

1. Simultaneous smoke measurements can be made of a wide variety of species with good selectivity (i.e. resistance to interference) over a wide range of concentrations with detection limits in the low ppbv range.
2. Measurements can be real time so that dynamic processes can be followed.
3. There is no need to take samples and no possibility of sampling- or storage-related artifacts so that reactive gases can be quantified.
4. The measurement is path integrated, averaging over small-scale local variations. It is thus relatively immune to spatial variation compared with point sampling.
5. Unanticipated species can be located and identified by screening spectra.

We have pioneered the application of the OP-FTIR technique to biomass fires. In this paper we review results from our in-situ studies of biomass fires carried out both in the field and the laboratory emphasizing the new contributions made by this technique.

Experimental Details

Fire-types investigated

The field measurements were made during prescribed burns in sagebrush (Wyoming) and coniferous forest activity fuels (Montana) as described in detail in *Griffith et al.*, [1991]. The first laboratory fires included two fires each of brown ponderosa pine needles and freshly cut sagebrush, two simulations of forest-floor ground fire in a coniferous forest, a low-intensity crown fire simulation, slash pile fire, and a broadcast burn simulation. These fires are described in detail in *Yokelson et al.*, [1996a]. With our new system we have studied fires in pine needles and sagebrush and we have expanded the fuel types to include rough fescue, wire grass, poplar wood shavings, gallberry leaves and stems, aspen bark, brown, partially-decomposed maple leaves, banana leaves, decomposed Ponderosa pine wood (lignin content 66.4%), cattails, palmetto, and organic soil and duff samples which were removed intact from ecosystems throughout the United States [*Yokelson et al.*, 1996b]. Also presented here are preliminary results from a recent series of experimental fires which have not yet appeared elsewhere. These fires include brown pine needles, brown pine needles with wind, brown pine needles with wind and diammonium phosphate (fire retardant), a vertically oriented green Douglas fir, and whole sagebrush plants.

Some fire behavior considerations for sampling programs

There are some aspects of fire behavior which must be considered in order to ensure the most representative sampling of the emissions. Flaming combustion of biomass fuels primarily produces highly oxidized compounds such as CO_2, NO_x, and SO_2. Smoldering combustion is a complex mix of fuel pyrolysis, small flames, and glowing combustion of char. These processes can accompany flaming or occur in varying combination after flaming and they produce many less-oxidized gaseous emissions of considerable interest to atmospheric chemists [*Lobert et. al.*, 1991; *Yokelson et al.*, 1996a, b]. Flaming combustion

not only produces different compounds from the other combustion processes, but it is associated with significantly larger fire-driven vertical convection velocities. This means rigorous fire-integrated measurements of production amounts or emission ratios should be "flux-based" as in (1)

(1) $P_i = \int_t c_i(t)\, f(t)\, dt \quad \cong \quad \Sigma_t\, c_{it} \times f_t \times \Delta t$

In (1) P_i, the production of species *i*, is the integral of the flux of species *i* over time and the flux of *i* is the product of the concentration ($c_i(t)$) and the fire-driven, volume flow (f(t)). In practice, P_i must be approximated from point measurements of concentration and flow as shown. In the laboratory, the option exists to provide an additional flow which is much larger than the fire-driven flow so that the flow is to a good approximation constant. Under these conditions only, a fire-integrated emission ratio can be computed as below.

(2) $P_i/P_j = (\Sigma_t\, c_{it})/(\Sigma_t\, c_{ij})$

In addition, mixing ratios can be used in place of concentrations in (2) to calculate emission ratios, if temperature and pressure are also held constant (which we have done in some laboratory experiments).

Description of spectrometers and auxiliary optics

Two different spectrometers have been used with three different types of auxiliary optics to perform the experiments reviewed here. The first measurements were made in 1989 on field fires in Montana and Wyoming using a collimated IR source up to 200 m distant from the collection optics and spectrometer [*Griffith et al.*, 1991]. The Fourier transform spectrometer (EOCOM) consisted of a Michelson interferometer, Ge/KBr beamsplitter, and an InSb/MCT detector. The instrument was operated at a spectral resolution of 0.12 cm-1 and a temporal resolution of 0.5 to 4 minutes. This apparatus was also used in 1989 in the Intermountain Fire Sciences Laboratory (IFSL) controlled-environment, combustion facility as summarized next [*Yokelson et al.*, 1996a]. The fuels were burned on a ca. 1 x 2 m continuously-weighed fuel bed, and the smoke captured by a 1.6 m diameter stack with a 3.6 m inverted funnel opening just above the fuel bed as shown in Figure 1a. A sampling platform surrounds the stack 15 meters above the fuel bed. The IR light source was collimated and transmitted twice across the stack

through the smoke for a total smoke absorption path of 3 m, then focused and re-collimated into the EOCOM spectrometer described and operated as above.

A new spectrometer and auxiliary optics were recently obtained to continue our optical fire emission measurements. In this system, the IR radiation from the FTIR (MIDAC model 2500) is directed through a 1.6 m basepath open White cell (I. R. Analysis), and then refocused on an external "wideband" MCT detector (Graseby FTIR M-16). (See Figure 1b.) The White cell allows long path lengths to increase absorption levels (up to 76.5 m in the experiments reported here) and directing the IR beam through the interferometer before the long, open, atmospheric path reduces measurement noise and interference due to emission from the hot gases *[Hanst and Hanst*, 1994]. The spectrometer was configured for a scan speed (and maximum time resolution) of 3 seconds at the spectral resolution of 0.5 cm^{-1} used in all measurements reported here. The spectrometer and White cell are co-mounted on a Super-Invar™ (Carpenter Inc.) structure and the mirror substrate has the lowest available thermal expansion (ULE™ (ultra-low expansion) Corning Inc.). The new system has been deployed on the IFSL sampling platform, at various other heights directly over smaller fires, and in a variety of specialty applications as described elsewhere [*Yokelson et al.*, 1996b].

In the laboratory experiments, smoke temperature was measured by chromel-alumel thermocouples verified to be accurate within 0.1 °C at the freezing and boiling temperature of water. Pressure (~ 90.2 kPa) was measured by the built-in pressure sensor in the Licor (model 6262). Stack flow was measured by a Kurz (model 455) mass flowmeter. Total fuel bed mass was logged every second using either one or two Mettler PM34 digital scales. CO_2 and CO were simultaneously measured by non-dispersive IR and NO and NO_2 were simultaneously measured by chemiluminescence monitoring. Fuels were subsampled for fuel moisture measurement and replicate measurements of the C:H:N content by a Perkin-Elmer Model 2400 CHN analyzer.

Spectrum analysis

Several different methods were used to retrieve concentrations from spectra. In general, to provide efficient processing of congested smoke spectra acquired at many different temperatures we have coupled the techniques of synthetic calibration [*Griffith*,

1996] and classical least squares fitting (CLS) [*Haaland*, 1990] to accomplish the bulk of the analysis. The computer program MALT (Multiple Atmospheric Layer Transmission) [*Griffith*, 1996] computes ideal spectra from HITRAN [*Rothman et al.*, 1992] absorption line parameters; convolves these spectra with the instrument function such that the calculated spectra closely match real experimental spectra; and generates a set of calibration spectra over a range of gas concentrations for multicomponent quantitative analysis using CLS methods. This eliminates the need to acquire reference spectra for a large number of compounds at many temperatures, rigorously deconvolves the multicomponent spectra, and is readily automated to decrease analysis time. In summary, MALT/CLS allows rapid, accurate analysis of any of the 35 molecules in the HITRAN data base, at arbitrary concentration, temperature, and pressure. For species for which spectral line parameters are not available, MALT/CLS cannot be used and more traditional methods are required including spectral subtraction and peak height based retrievals. Full details of all the analysis methods can be found elsewhere [*Griffith et al.*, 1991; *Griffith*, 1996; *Yokelson et al.*, 1995, 1996a, b].

Accuracy and detection limits

The nominal accuracy of both the molecular line parameters in HITRAN and our reference spectra is 5% or better [*Rothman et. al.*, 1992; *Hanst and Hanst*, 1994]. The precision and accuracy of our MALT/CLS data are indicated by plotting against each other the concentrations retrieved for the same molecule in the same spectrum, but from different spectral regions. For example, we measure ammonia and formaldehyde (two important gases which are especially difficult to measure with conventional sampling methods) in three separate spectral regions each with our IR technique. The analyses from different regions typically have better than 3 % precision as shown in Figure 2. We have also satisfactorily intercompared the FTIR concentration data with that simultaneously obtained by other instruments when possible [*Yokelson et al.*, 1995a, b] Based on these tests and others, we estimate the uncertainty in the individual concentration measurements as $\leq$ 10 % (1σ) or the detection limit; whichever is greater. This implies an uncertainty in the emission ratios of $\leq$ 14 % (1σ). The detection limits are different for each species and

for each spectrum, but are normally in the low "tens" parts per billion, or better, when long (ca. > 70 m path lengths are used) .

Results

Time series of concentrations of up to twenty-one compounds could be determined for these fires. These compounds were (in rough order by production levels) water, carbon dioxide, carbon monoxide, and methane, then roughly equal amounts of formaldehyde, methanol, acetic acid, nitric oxide, ammonia, and ethene, and then at lower (more variable) levels nitrogen dioxide, sulfur dioxide, 2-hydroxyethanal, phenol, formic acid, hydrogen cyanide, carbonyl sulfide, ethane, ethyne, propene, and mixed volatile higher hydrocarbons. Figure 3 shows typical results for concentration time series for selected compounds arising from the different combustion processes occurring in a fire in a bed of Ponderosa pine needles. The fire-integrated results were derived from the time series and flow measurements as discussed earlier and have been presented in tables elsewhere [*Griffith et al.*, 1991; *Yokelson et al.*, 1996a, b]. The preliminary results from the recent series of large-scale fires have not yet been presented elsewhere and are given in full in Table 1. Table 2 presents the overall average results from each study in the same format to facilitate comparison.

Discussion

Earlier laboratory studies of *Lobert et al.* [1991] were carried out in homogeneous fuels. That work demonstrated that some compounds can be attributed to flaming or smoldering combustion based on a linear correlation with CO_2 or CO, similarity of the normalized temporal profile with CO_2 or CO, and degree of oxidation. Our results confirm some of these observations. The normalized temporal profiles for selected flaming and smoldering compounds can be seen in Figure 3 (a) and (b).

However, we also measure significant amounts of compounds that do not correlate linearly with either CO_2 or CO and show markedly different normalized temporal profiles (Figure 3 (c)). These compounds are known biomass pyrolysis products contained in white smoke produced by heating of the primary fuel [*Shafizadeh et al.*, 1976; *Overend et al.*, 1985; *Evans et al.*, 1986; *DeGroot et al.*, 1988; *Yokelson et al.*, 1996a, b]. Pyrolysis

products that we quantify are acetic and formic acid, methanol and phenol, formaldehyde and 2-hydroxyethanal, light unsaturated hydrocarbons, hydrogen cyanide and carbonyl sulfide.

The difference in the products arising from pyrolysis and glowing combustion and the potential for smoke composition to change rapidly is illustrated in Figure 4. Figure 4(a) shows the same spectral region (the "fingerprint" region) from two different spectra acquired at different times during the same fire in thin hardwood fuel. The top trace is of the fire products when white smoke and glowing combustion coexist just after the cessation of flames. The bottom trace was acquired ~ 50 s later, when only glowing combustion, with no visible smoke production, was observed. As indicated in Figure 4 (a), the top ("white smoke + glowing") trace is dominated by the features of acetic acid, formic acid, methanol, ethene, and 2-hydroxyethanal, but also includes smaller features due to NH_3 and CH_4. In contrast, the "fingerprint" trace of the glowing emissions is remarkably simple and consists almost entirely of NH_3 and CH_4 features. Another region of these same two spectra, the "C-H stretch" region (2700 - 3100 cm^{-1}), is shown in Figure 4 (b). The "C-H stretch" trace shows H_2CO and heavy NMHC's only in the (top) "white smoke + glowing" trace. In the "smokeless glowing" trace the C-H stretch region only shows strong features due to CH_4, and weak features due to C_2H_6. We have also conducted OP-FTIR "temperature ramp" experiments [*Yokelson et al.*, 1996b] to isolate the pyrolysis process and determine that "pure white smoke" does not contain NH_3 and CH_4.

The bulk of previous smoke characterization has relied upon gas chromatography with a flame ionization detector (GC/FID) as the analytical technique. GC/FID, as implemented in these studies, is capable of detecting only three of the compounds shown in Figure 4 (methane, ethane, and ethene) and thus that technique would be incapable of elucidating the dramatic change that occurred in smoke composition or of identifying the processes from which the emissions originate. Thus, this figure illustrates the great value of OP-FTIR for providing an overview of smoke composition and for relating the observed phenomena to the fundamental combustion processes and the resulting emissions.

In summary, fire emissions are due to a combination of at least three very different, temporally-overlapped combustion processes. Each process produces its own mix of emissions (including some reactive gases) and the relative weighting of these processes can sometimes change rapidly leading to a rapid change in smoke composition. The black smoke associated with flaming consists primarily of CO_2 and other highly oxidized compounds [*Lobert et. al.*, 1991; *Ward and Radke*, 1993; *Yokelson et. al.*, 1996a] as well as carbonaceous aerosol [*Radke et al.*, 1991]. In contrast, the white smoke produced by heating fresh fuel is rich in pyrolysis products (such as formaldehyde, 2-hydroxyethanal, methanol, phenol, and organic acids) and (probably) "distillation" products such as "heavy hydrocarbons" [*Yokelson et al.*, 1996b]. Glowing combustion, in the absence of visible flames or smoke, did not produce oxygenated compounds or "heavy hydrocarbons," but did produce a good deal of excess CO_2, CO, CH_4, and NH_3 [*Yokelson et al.*, 1996b]. The CO_2 and CO (the major emissions of "smoldering combustion") probably arise predominantly from gasification of char which includes the following reactions [*Hshieh and Richards*, 1989; *Kannan and Richards*; 1990].

(3) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

(4) $C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)}$

Production of oxygenated organic compounds

Comparison of the production levels measured by OP-FTIR for various emissions with results from other techniques has proved useful. This comparison is especially important for the difficult to measure oxygenated organic compounds for which relatively little other data has been available [*Yokelson et al.*, 1996a]. Here we review the comparison for acetic acid. *McKenzie et al.* [1995] measured organic acids from laboratory fires with coniferous fuels by cryotrapping and GC/MS analysis, while three other studies used the mist chamber technique [*Cofer et al.*, 1985] for organic acids: *Talbot et al.* [1988] from brush and hardwood fuels in laboratory studies, *Dinh et al.* [1991] from African savannah fires, and *Lacaux et al.* [1994] from African charcoal-making kilns. It is possible to make a limited comparison between our measurements and these other results if we normalize for fire-type as explained next. The relative mix of combustion processes which can occur in a whole fire varies continuously across a spectrum. A useful index of the relative amount of

flaming and smoldering occurring in a fire is the modified combustion efficiency (MCE) defined as $\Delta CO_2/(\Delta CO_2 + \Delta CO)$ [*Ward and Radke*, 1993]. Emission production can be plotted versus MCE and a linear correlation is often obtained for results from a wide variety of fire or combustion conditions. In Figure 5 we show our OP-FTIR data for acetic acid with the other published measurements which include sufficient auxiliary data to estimate MCE. In summary, Figure 5 indicates that our data show good internal consistency (i.e. strong correlation of emission factors with combustion efficiency) while all other measurements show much lower emission factors and little or no correlation with combustion efficiency.

No previous measurements exist for another oxygenated organic molecule, 2-hydroxyethanal, which was observed in smoke for the first time by our OP-FTIR technique [*Yokelson et al.*, 1996b]. Our work showed that this compound can account for up to ~ 1% of the carbon (by mass) detected in the emissions. Observation of high levels of this compound is not surprising as 2-hydroxyethanal is often the dominant product that arises from heating cellulose [*Richards*, 1987; *Radlien et al.*, 1991].

In general our OP-FTIR work indicates production levels for oxygenated organic compounds which are 5 to a 1000 times higher than other work. This is significant since these compounds are likely to impact plume chemistry, perhaps by serving as an early source of oxidants. Unlike fossil fuels, biomass is about 45 % oxygen. Thus, oxygenated organic compounds are important as initial emissions in addition to their traditionally recognized importance as secondary products from the oxidation of hydrocarbons.

Production of nitrogen and sulfur compounds

It is also instructive to compare OP-FTIR measurements of nitrogen-containing compounds with other work. The dominant nitrogen-containing emissions we measure are NO and NO_2 from flaming and NH_3 from smoldering combustion. A nitrogen mass balance was calculated for fires in brown pine needles. NO, NO_2, and NH_3 accounted for 38%, 4%, and 13% of the fuel nitrogen respectively, a total of 55%. Emitted N_2O and CH_3CN were below detection limits, and other nitrogenous compounds such as HCN were observed only at low levels for aboveground biomass. Accepting the value of *Kuhlbusch et al.*, [1991] of 36 ± 13% for N_2 emission, and a value of 10% for ash nitrogen [*Hurst et al.*, 1994; *Crutzen and Andreae*, 1990], these emission factors account

for all the fuel nitrogen within the experimental uncertainties. These findings are in general agreement with *Hurst et al.,* [1994] who report high levels of NO, NO_2 and NH_3 and that N_2O, HCN and CH_3CN each account for less than 1% of the fuel nitrogen. *Lobert et al.*, [1991] were the first to present extensive speciation of nitrogen compounds. They reported higher levels of HCN, nitrates, nitriles, and amines than the above studies. For all studies the partitioning of NH_3 and NO_x as a function of MCE seems remarkably consistent and is shown in Figure 6.

Our experiments reported the first measurement of a tar (condensed products) yield [*Yokelson et al.*, 1996b]. The tar yield for fires was measured twice at ~ 1.2 % by mass, but the tar was also measured to be 6 to 7 times richer in N than the parent material. (Gentle heating of the tar at 58 °C produced NH_3 as well as acetic acid and heavy hydrocarbons.) The nitrogen contained in the tar in our experiments probably accounts for some of the nitrogen measured in ash in other work.

In contrast to the above results, for the specific case of organic soils, we found that the HCN/NH_3 ratio varied by about two orders of magnitude. For a fire in a sample of North Carolina bog soil, HCN production actually dominated ammonia production by a factor of five. Steam distillation of soil nitrates is a source of NH_3 [*Stevenson*, 1982] and consistent with this, there was a tendency for the drier soils to produce a higher HCN/NH_3 ratio. A systematic study of this effect is planned.

The only sulfur compound we reported from belowground biomass was carbonyl sulfide and fuel sulfur content was not measured. OCS emissions from organic soils correlated with *soil nitrogen* contents ($r^2 = 0.87$) suggesting that sulfur and nitrogen content are correlated in our soil samples.

Speciation of hydrocarbons

Numerous studies have used canister sampling followed by GC/FID analysis to measure the speciation of C_2 - C_4 non-methane hydrocarbons ("light" NMHC's) in smoke. There are no previous measurements of the amounts of monoterpene compounds (C_{10}) in smoke, but these compounds could significantly affect plume chemistry through their fast gas-phase reactions with OH and O_3. For this reason we are currently working on estimates of the fire production of these compounds. In principle, for any air parcel, the

spectral region from 2700 - 3100 cm^{-1} (the C-H stretch region) will have a characteristic shape that reflects the overall blend of hydrocarbons in that air parcel. The C-H stretch spectrum of biomass fire smoke, regardless of the biomass burned, exhibits a continuum which peaks near 2930 cm^{-1} and is similar in appearance to the C-H stretch spectra of monoterpenes [*Yokelson et al.*, 1995]. (See also Figure 4b.) The preliminary indication from the data that we have to date is that monoterpenes could actually be more abundant than the commonly reported light NMHC's.

Management/mitigation strategies

A goal of our research is to develop strategies which will allow realization of the land management benefits of fire while minimizing adverse atmospheric impacts. We are making good progress in understanding the different types of combustion and resulting smoke composition and we are noting firing techniques which can promote specific types of combustion. An example of this progress can be seen in Figure 6. Figure 6 shows that burning under conditions which favor smoldering combustion would also favor emitting the fuel nitrogen to the atmosphere as NH_3 instead of NO_x. NO_x is a precursor for tropospheric O_3 and acid rain while NH_3 can actually neutralize atmospheric acids. However, promoting smoldering combustion will have numerous other effects. In addition, the local state of the atmosphere will also greatly impact the fate of the emissions. Therefore, careful atmospheric modeling and field validation will be required to understand the effects of different fire-types and emissions-processing scenarios.

Estimates of initial emissions for atmospheric models

Our results to date show clearly that different fire-types can emit quite different compounds. In addition, the initial emissions typically vary throughout a single fire [*Lobert et al.*, 1991; *Yokelson et al.*, 1996a, see Figures 4 - 6] and (except for CO_2 and CH_4) most of the dominant biomass fire emissions are too reactive to be well mixed in the global troposphere [*Prather et al.*, 1994]. Therefore the influence of individual fires could vary strongly depending on the fire-type and the state of the atmosphere. We are initiating detailed, microscale modeling of fire plumes to investigate these and other effects.

Larger-scale models, including long-range transport, have made important contributions in linking fire emissions to regional tropospheric chemistry [*Chatfield and*

Delaney, 1990; *Richardson et al.*, 1991; *Keller et al.*, 1991; *Crutzen and Carmichael*, 1993; *Chatfield et al.*, 1996]. In these larger efforts, the emissions resulting from many fires burning simultaneously are modeled and a reasonable estimate of fire-averaged emissions is of use. A simple method for estimating the initial concentrations in these models relies on the observation that most compounds (as a first approximation) are emitted proportional to CO or CO_2. Table 2 summarizes all the in-situ spectroscopic data as such a ratio. The data in Table 2 must be combined with data from other sources such as GC/FID data for hydrocarbons, GC/ECD data for halogenated organics, and the H_2 data of *Cofer et al.* [1988;1990]. All our spectroscopic work is consistent with the following summary of fire-integrated emissions. CO_2, CO, and CH_4 are the three dominant emissions and a fourth "tier" (just below methane) includes methanol, acetic acid, formaldehyde, ethene, ammonia and nitric oxide.

Conclusions

OP-FTIR has contributed significantly both to smoke characterization and probing of the process-level origin of emissions. As a result, a new picture of smoke composition has emerged (with higher levels of oxygenated organic compounds) which should be integrated into plume chemistry models. The OP-FTIR work shows that nearly all fuel nitrogen in aboveground biomass can be accounted for with a few measurements; NH_3, NO_x, N_2, and ash nitrogen. Future FTIR work will include airborne measurements to probe transport and transformation details and to assist in validating next-generation smoke models.

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Figure Captions

Figure 1. (a) Simplified illustration of the IFSL combustion lab (not to scale). The EOCOM FTIR was located at "A" in the first laboratory study and the MIDAC/White cell system has been deployed at both "A" and "B" in current work. (b) Schematic diagram of the new MIDAC/White cell system (not to scale).

Figure 2. In each plot the concentrations derived for a compound from MALT/CLS analysis of three independent regions of the same spectra are plotted versus each other (see text). (a) shows the concentrations from three regions for formaldehyde while (b) shows results from three regions for ammonia.

Figure 3. Examples of time evolution of compounds emitted from a fire in a fuel bed of pine needles separated by (a) flaming, (b) smoldering, and (c) pyrolysis/distillation combustion process.

Figure 4. (a) The top trace shows the "fingerprint region" of a smoke spectra from a fire in thin hardwood fuel elements that is producing white smoke at the same time that glowing combustion is observed. The bottom trace is the same spectral region for the same fire ~ 50 s later when white smoke production has ceased and only glowing combustion is observed. The top (white smoke + glowing) trace is dominated by strong features due to the indicated oxygenated organic compounds. The lower (glowing only) trace shows features due to CH_4 and NH_3 only. (CO_2 and CO features are present in both traces in a spectral region not shown here.) (b) As in (a) except that the spectral region shown is the "C-H stretch" region. Sharp features due to H_2CO and a continuum consistent with the presence of monoterpenes are found only in the (top) "white smoke + glowing spectrum." In the lower "glowing only" trace, all strong features are due to CH_4 and weak ones are due to C_2H_6.

Figure 5. Acetic acid emission factors as a function of modified combustion efficiency. The regression equations are for the FTIR results. The results of *Talbot et al.*, and *Lacaux et al.*, are from studies using the mist chamber technique. The results of *McKenzie et al.*, are based on GC/MS.

Figure 6. Fire-integrated NH_3/NO_x molar ratios as a function of modified combustion efficiency for all laboratory fires studied by OP-FTIR compared with other studies. *Radke*

et al., [1990] report a mass of NO_x, which is represented as a 50:50 mixture of NO and NO_2 and the error bar shows the range of possible values due to changing this ratio.

Table 1. Preliminary emission results for recent series of fires (see text) expressed as 100 X moles compound/moles total carbon detected.

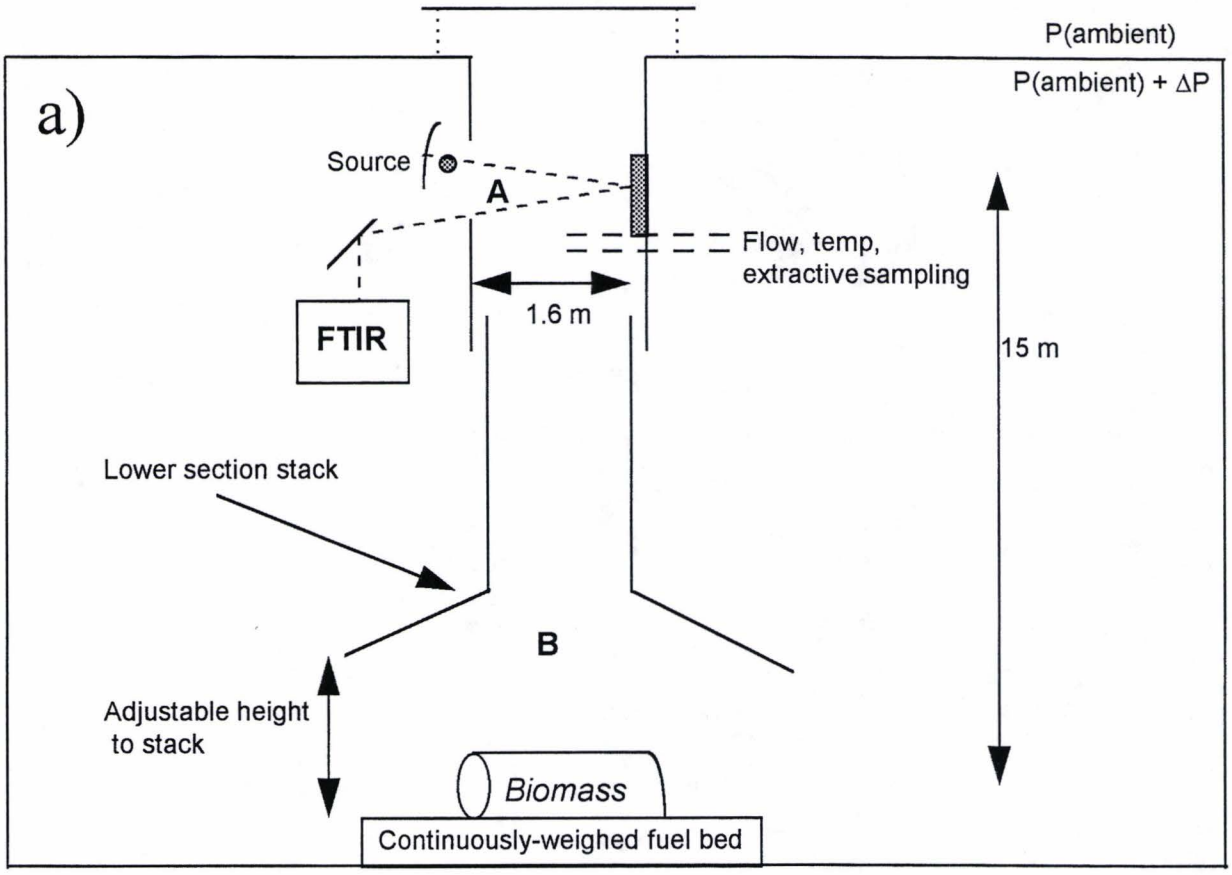
Fire/Fuel	CO_2	CO	CH_4	NO	CH_2O	C_2H_4	NH_3	CH_3OH	CH_3COOH	HCOOH
Ponderosa pine needles (PPN)	94.34	5.20	0.207	0.172	0.054	0.078	0.061	0.023	bld	0.022
PPN with wind	93.63	5.90	0.215	0.081	0.062	0.077	0.070	0.037	bld	bld
PPN with wind and fire retardant	92.27	6.57	0.678	0.104	0.059	0.080	0.096	0.113	0.075	bld
Sagebrush	93.03	5.98	0.474	0.148	0.117	0.066	0.092	0.098	0.082	bld
Douglas Fir (vertical orientation)	93.44	5.89	0.266	0.128	0.112	0.092	0.102	0.019	0.027	0.032
Poplar shavings	94.39	4.59	0.356	0.087	0.124	0.114	0.066	0.124	0.072	0.045
Average all fires	93.52	5.69	0.366	0.120	0.088	0.085	0.081	0.069	0.064	0.033

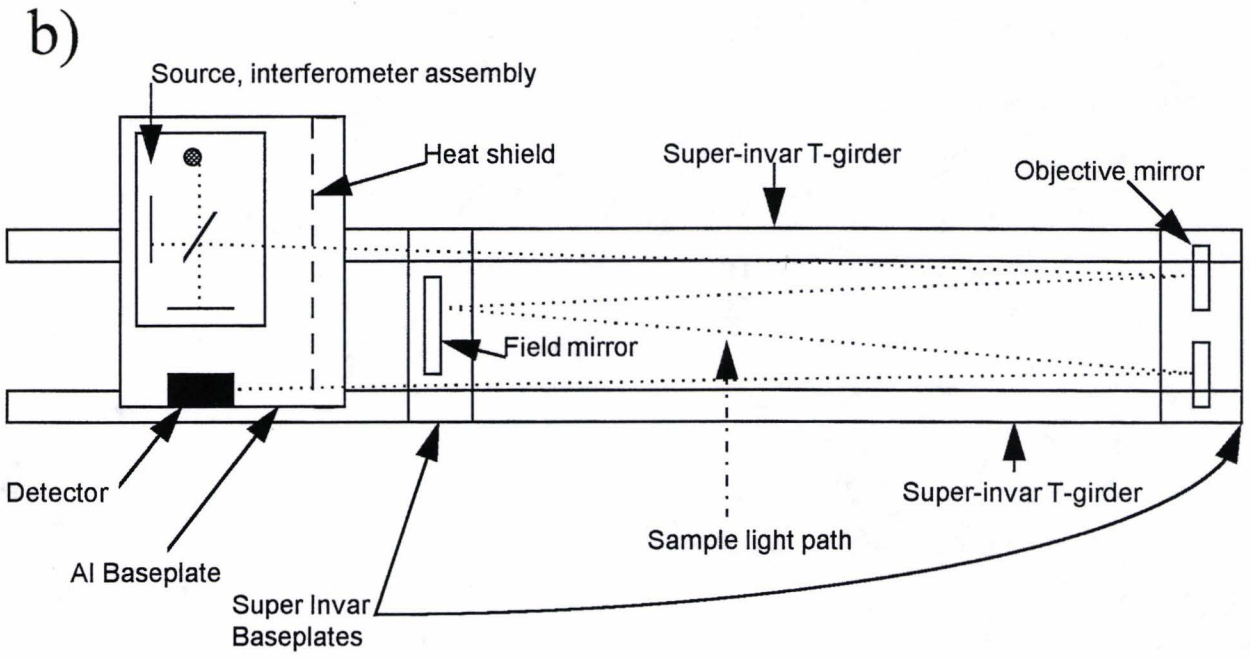
Table 2. A summary of *in-situ,* spectroscopic, biomass fire emission measurements expressed as percentages of CO_2 and CO.

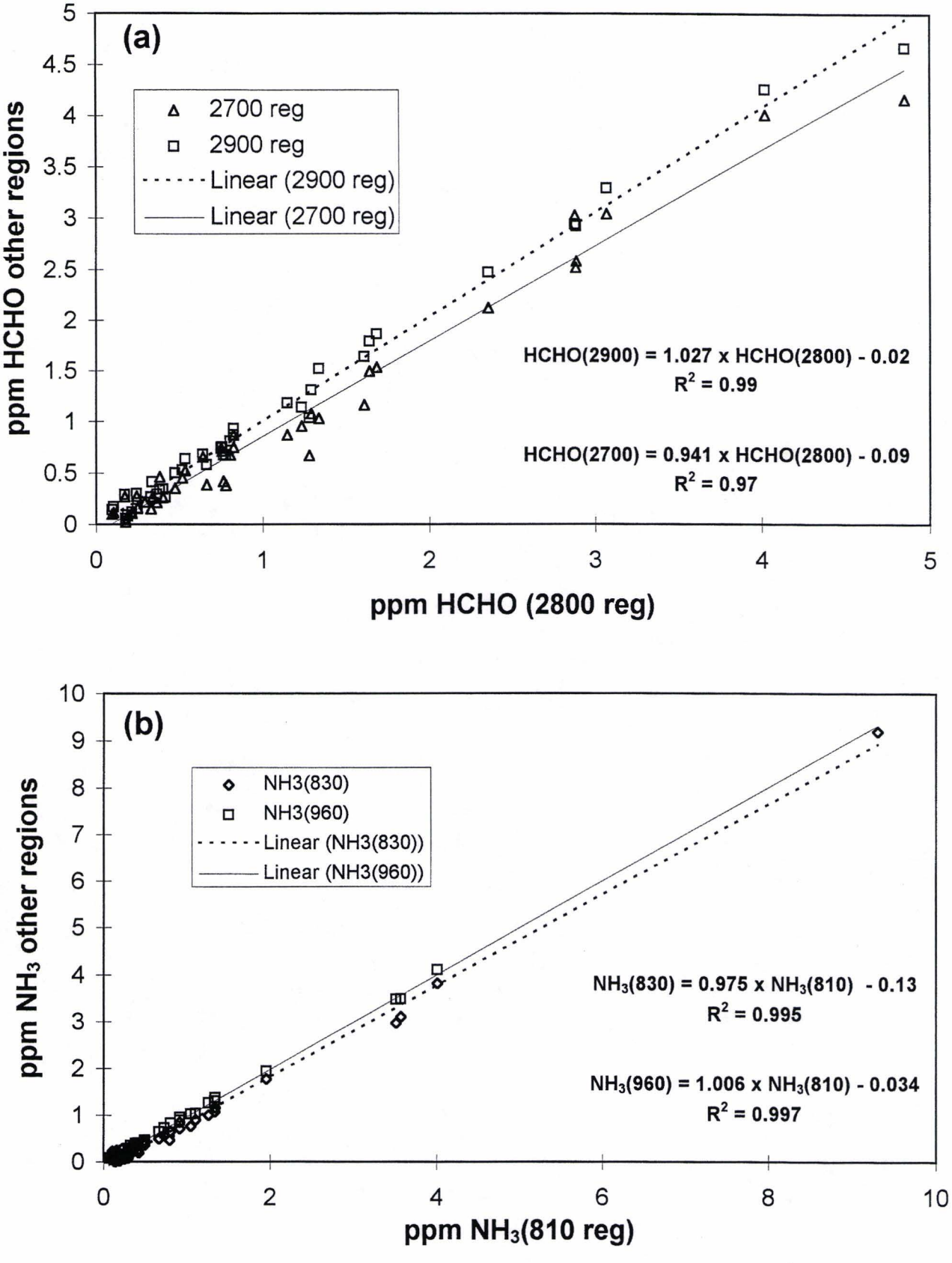
Study	Emissions as percent of CO_2		
	NO	SO_2	NO_2
Griffith et al., 1991	0.095	nm[1]	0.050
Yokelson et al., 1996a	0.178	0.063	0.050
This work[2]	0.128	nm	nm

	Emissions as percent of CO													
	Hydrocarbons					Aldehydes		Acids		Alcohols		Nitrogen[3]		Sulfur
	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	HCHO	Glycol-	Formic	Acetic	CH_3OH	C_6H_6O	NH_3	HCN	OCS
Griffith et al., 1991	7.61	nm	nm	nm	nm	1.27	nm	nm	nm	nm	nm	3.24	0.12	nm
Yokelson et al., 1996a	10.86	1.42	1.71	0.98	nm	1.60	nm	0.73	2.32	1.61	nm	1.91	0.44	nm
Yokelson et al., 1996b	6.55	0.45	0.98	0.17	0.65	2.33	1.08	1.09	2.20	1.98	0.84	2.66	0.65	0.04
This work	6.43	nm	1.49	nm	nm	1.55	nm	0.58	1.12	1.21	nm	1.42	nm	nm
Average published	8.34	0.94	1.35	0.57	0.65	1.73	1.08	0.91	2.26	1.80	0.84	2.60	0.40	0.04

[1]nm, not measured.
[2]This work refers to preliminary results from recent fires described in text.
[3]If fuel N data is available Figure 6 can be consulted to partition NH_3 and NO_X.


a)
P(ambient)
P(ambient) + ΔP
Source
A
Flow, temp,
extractive sampling
1.6 m
15 m
FTIR
Lower section stack
B
Adjustable height
to stack
Biomass
Continuously-weighed fuel bed


b)
Source, interferometer assembly
Heat shield
Super-invar T-girder
Objective mirror
Field mirror
Detector
Al Baseplate
Super Invar
Baseplates
Sample light path
Super-invar T-girder


(a)
2700 reg
2900 reg
Linear (2900 reg)
Linear (2700 reg)
HCHO(2900) = 1.027 x HCHO(2800) - 0.02
R2 = 0.99
HCHO(2700) = 0.941 x HCHO(2800) - 0.09
R2 = 0.97
ppm HCHO other regions
ppm HCHO (2800 reg)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0
1
2
3
4
5

(b)
NH3(830)
NH3(960)
Linear (NH3(830))
Linear (NH3(960))
NH3(830) = 0.975 x NH3(810) - 0.13
R2 = 0.995
NH3(960) = 1.006 x NH3(810) - 0.034
R2 = 0.997
ppm NH3 other regions
ppm NH3(810 reg)
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10

Figure 2

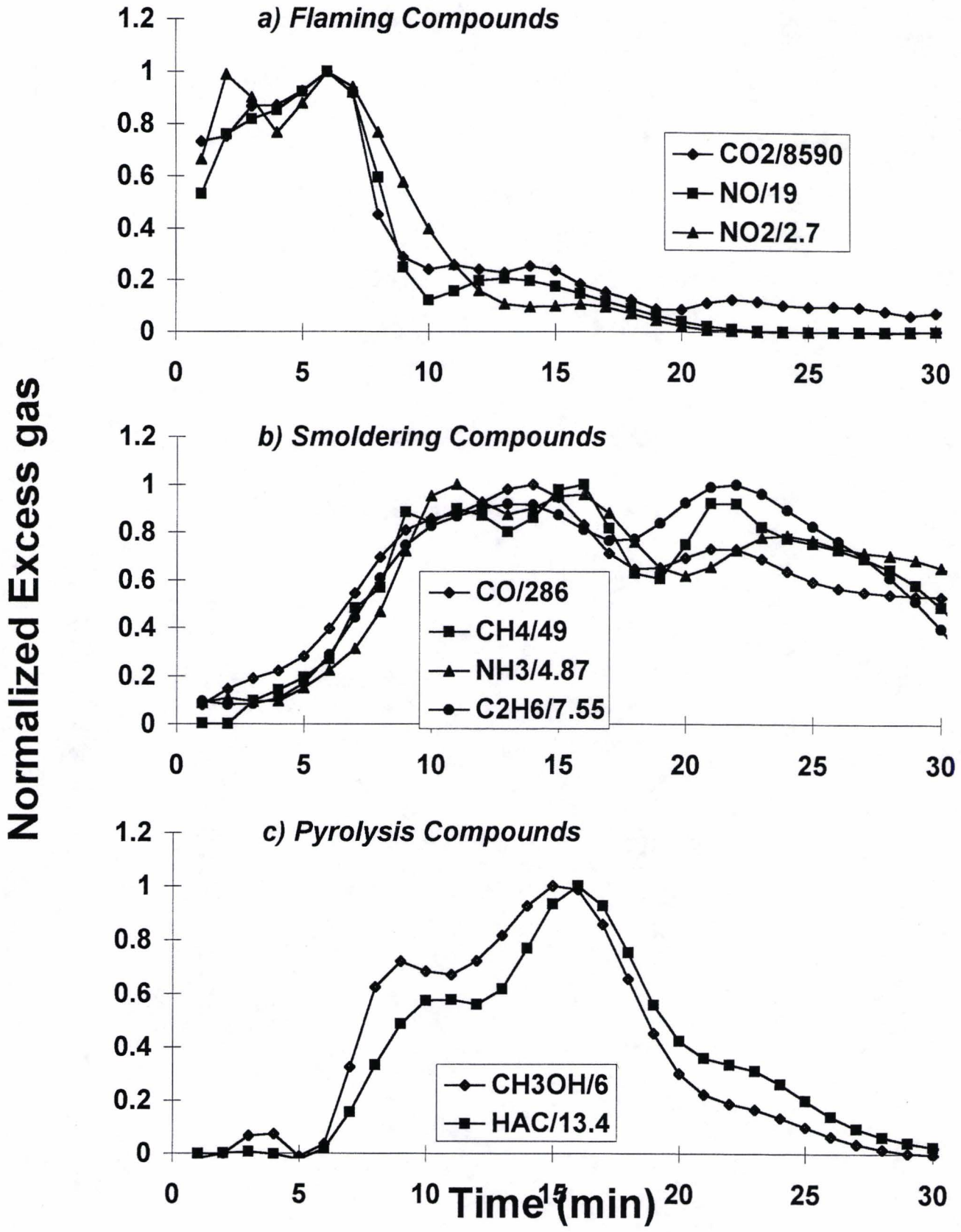

a) Flaming Compounds
CO2/8590
NO/19
NO2/2.7
b) Smoldering Compounds
CO/286
CH4/49
NH3/4.87
C2H6/7.55
c) Pyrolysis Compounds
CH3OH/6
HAC/13.4
Normalized Excess gas
Time (min)
0
0.2
0.4
0.6
0.8
1
1.2
0
5
10
15
20
25
30

Figure 3

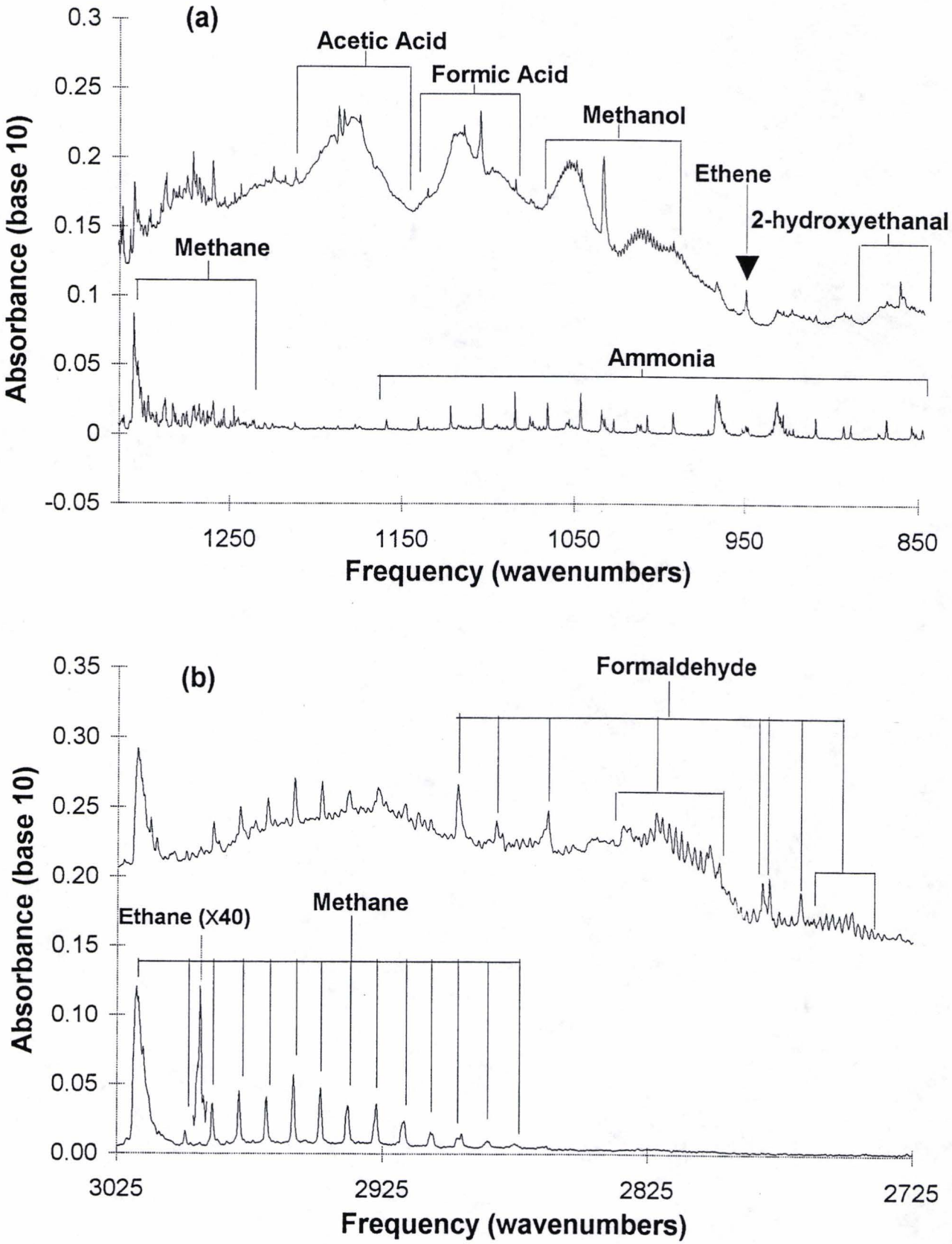

(a)
Acetic Acid
Formic Acid
Methanol
Ethene
2-hydroxyethanal
Methane
Ammonia
Absorbance (base 10)
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
1250
1150
1050
950
850
Frequency (wavenumbers)
(b)
Formaldehyde
Methane
Ethane (X40)
Absorbance (base 10)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3025
2925
2825
2725
Frequency (wavenumbers)

Figure 4

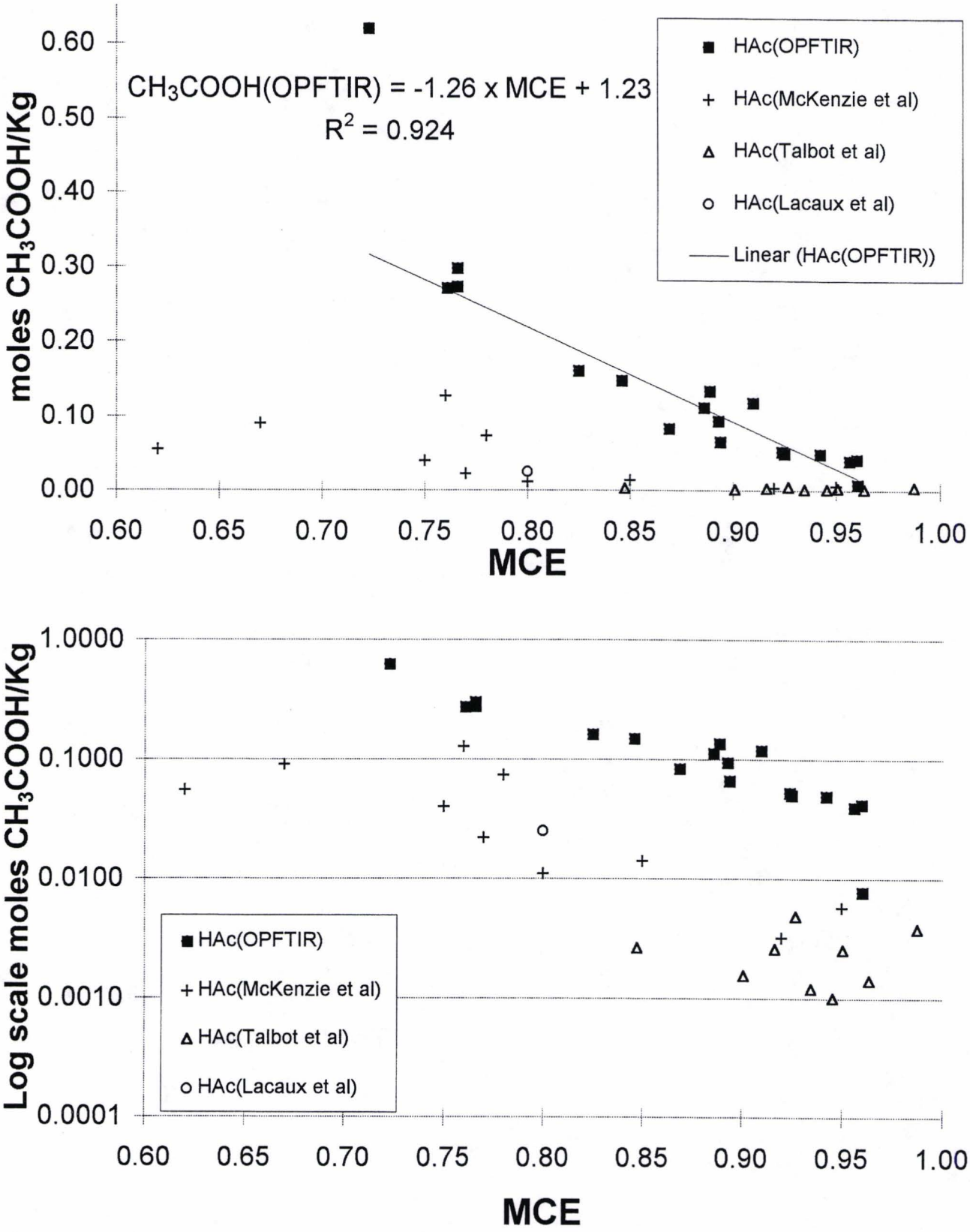

CH3COOH(OPFTIR) = -1.26 x MCE + 1.23
R2 = 0.924
HAc(OPFTIR)
HAc(McKenzie et al)
HAc(Talbot et al)
HAc(Lacaux et al)
Linear (HAc(OPFTIR))
moles CH3COOH/Kg
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00
MCE
Log scale moles CH3COOH/Kg
1.0000
0.1000
0.0100
0.0010
0.0001
HAc(OPFTIR)
HAc(McKenzie et al)
HAc(Talbot et al)
HAc(Lacaux et al)
0.60 0.65 0.70 0.75 0.80 0.85 0.90 0.95 1.00
MCE

Figure 5

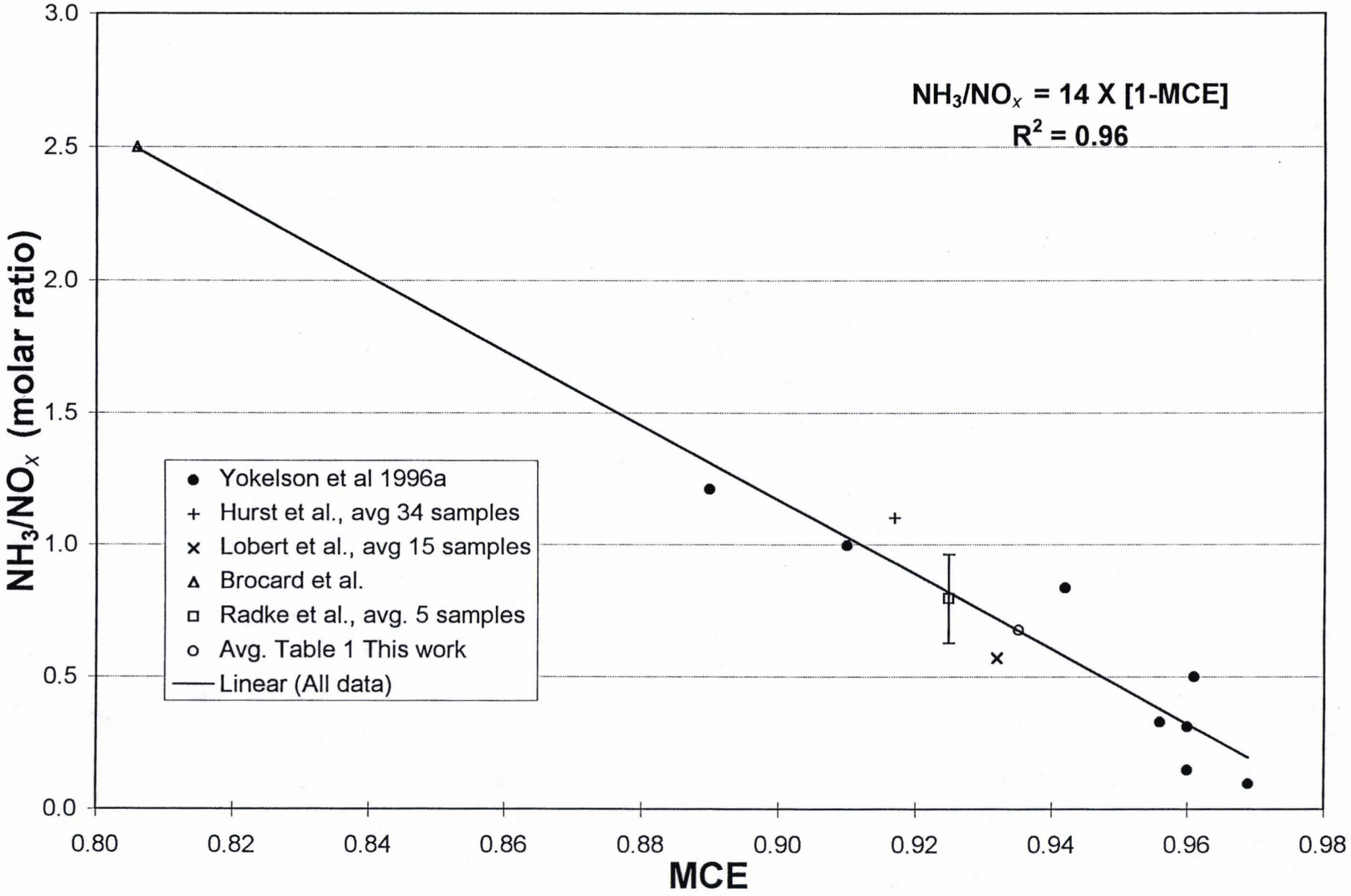

NH_3/NO_x = 14 X [1-MCE]
R^2 = 0.96
NH_3/NO_x (molar ratio)
MCE
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.80
0.82
0.84
0.86
0.88
0.90
0.92
0.94
0.96
0.98
Yokelson et al 1996a
Hurst et al., avg 34 samples
Lobert et al., avg 15 samples
Brocard et al.
Radke et al., avg. 5 samples
Avg. Table 1 This work
Linear (All data)

Figure 6

Progress In Smoke Characterization And Modeling

Darold E. Ward[1] and Robert J. Yokelson[2]

Abstract

The composition, dispersion, and health effects of smoke from biomass fires is being studied through a collaboration of the United States Forest Service and the University of Montana. Instrumentation for studying smoke composition includes gas chromatography, open-path Fourier transform infrared spectroscopy, nephelometers, and other techniques making it possible to analyze for hundreds of the constituents of smoke. Analytes include particulate matter (PM2.5), CO_2, CO, hydrocarbons, oxygenated and halogenated organic compounds, and nitrogen and sulfur compounds. This instrumentation has been deployed above controlled fires in our laboratory and in the field; or on aircraft probing individual fires and regional haze in the United States, Brazil, and Africa. Laboratory and tower deployments focus on detailed source characterization coupled with measurement of fire effects on soils. Data from laboratory, field, ground, and airborne sampling are being coupled with photochemical plume models. A comprehensive assessment of the health effects of smoke is also nearing completion. Future deployments of our instrumentation are planned for Southeast Asia as part of the SEAFIRE program.

Introduction

Humans have realized tremendous benefits from the use of fire for over 10,000 years. For example, plants produce enough biomass annually to meet the global energy demand 30 times over (Brink et al. 1976). In addition, biomass burning is an important component of shifting cultivation that supplies the nutrients needed to grow food for some 400 million people worldwide. With proper management practices, shifting cultivation can be sustained (Steinhart and Steinhart 1974); (Fehlberg 1989). Finally, many ecosystems around the world have evolved with fire as a dominant force, and land managers have long used controlled fire as a tool to promote forest health and reduce the risk of unwanted wildfire (Forest Service Southern Region 1989); (Goldammer and Penafiel 1990); (Stott et al. 1990).

However, improperly used, fire may have negative impacts. Land degradation may result if fires are too frequent or intense (Kauffman and Uhl, 1990); (Kauffman et al. 1994). Trace gas and particulate emissions from fires are generally pollutants and result in atmospheric effects that have been reviewed elsewhere (Crutzen and Andreae 1990); (Crutzen and Carmicheal 1993) and are summarized here. CO_2 and CH_4 are greenhouse gases (GHG) produced by biomass burning, and biomass fires may be responsible for up to 20% of the recent atmospheric buildup of these gases. Biomass burning can increase atmospheric GHG in two fundamental ways: through deforestation and through the occurrence of high-intensity fires in ecosystems not well-adapted to fire. Much of the

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carbon dioxide, accounting for 80-95% of fuel carbon (FC), released by fires may be eventually converted back to plant material through the process of photosynthesis. The pollutant CO (5-15% FC) consumes OH radicals (which "clean" the atmosphere). Methane (~ 1% FC) also consumes OH in addition to being a greenhouse gas. Oxygenated organic compounds (~ 1% FC) can be pollutants, precursors for the formation of OH, and contribute to acid precipitation. NO and NO_2 (0.5-2% FC) are pollutants, contribute to the acidity of precipitation, and react photochemically with non-methane hydrocarbons (~ 1% FC) to form tropospheric O_3 (which is itself a GHG and a pollutant). Halogenated hydrocarbons (~0.02% FC) may affect the concentration of stratospheric O_3. The particulate matter from fires (~ 1% FC) is a pollutant and may also cool the atmosphere (due to light scattering) possibly masking the effect of GHG buildup temporarily (Penner et al. 1992). In many areas, including Southeast Asia, fires have contributed to regional pollution episodes ("haze layers") for which the potential health effects are of concern (Other authors this volume). Obviously, quantitative measurements of fire effects on the land, initial emissions, the ability to forecast dispersion, and an understanding of atmospheric chemical transformation of smoke are all crucial to properly manage this important tool. The United States Forest Service has been studying many aspects of wildland fire; including the air quality impacts of controlled burning on local and regional communities (Ryan and McMahon 1976); (McMahon et al. 1980); (Ward et al. 1993). Research accomplished during this period has led to improvements in the management of smoke from planned fires (Southern Forest Fire Laboratory 1976). To understand the chemistry and physics that govern the coupled fire-atmosphere system, we divide the problem into two major areas:

- Quantifying the initial chemical composition of smoke.
- Quantifying the chemical and meteorological processes transforming the smoke.

It is our hope that continued research in these areas will promote more effective fire management.

Fire and Smoke Research Platforms and Instrumentation

Ground-Based Field Measurements

Our Fire Atmosphere Sampling System (FASS) was developed to characterize the initial chemical composition of smoke in the field and to simultaneously measure the flux of smoke from fires to the atmosphere (Ward et al. 1992). The FASS consists of instrumented towers (typically 5 - 15 m tall, see Figure 1) that are erected on the site of a planned burn before ignition and then collect data throughout the fire. (Some details of the FASS instrumentation are shown in Figure 1.) Real time measurements include temperature, three-dimensional winds, fire-driven vertical velocity, CO_2, CO, NO, and particulate concentration. Integrated measurements (by combustion type; i.e., flaming and smoldering) include particulate on filters and CO_2, CO, and hydrocarbons in stainless steel canisters. In particular, the real-time flow measurement should not be overlooked because flaming combustion injects its specific suite of products into the atmosphere at a much higher rate than smoldering combustion. The FASS instruments were specifically designed to be transportable as excess baggage.

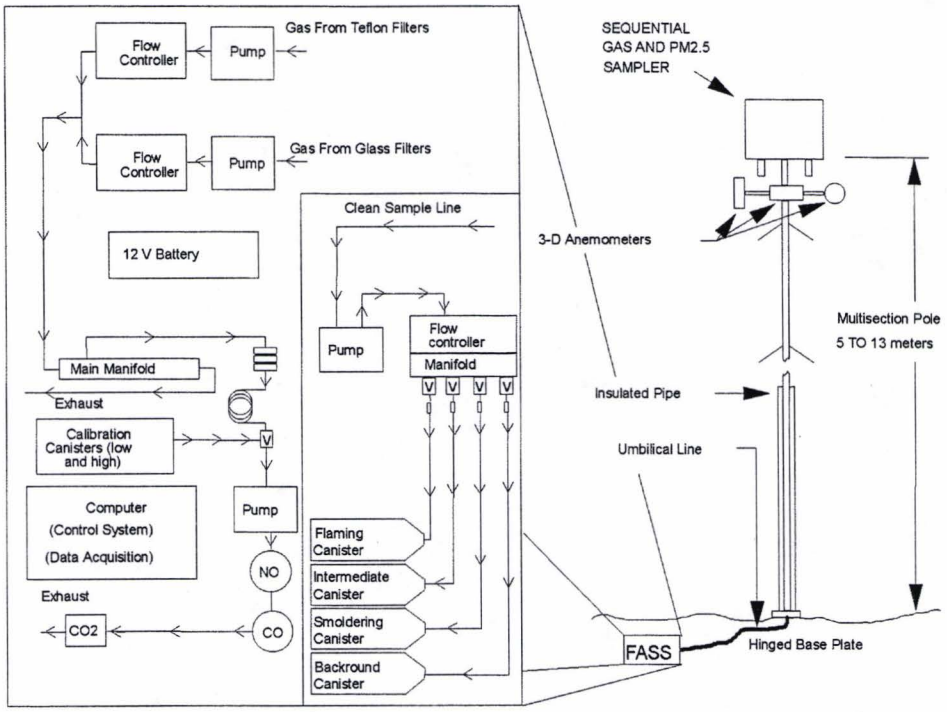

Figure 1. A schematic diagram of the fire-atmosphere sampling system (FASS).

The FASS has been deployed on controlled burns throughout North America, Brazil, and Africa, often in collaboration with simultaneous in-situ measurements of the fire effects on soils and fuel loading (Shea et al. 1996). Major activities involving the FASS in tropical countries include:

- Simultaneous airborne and ground-based measurements in the Rainforest and savanna fires in Brazil (Ward et al. 1992); (Ward et al. 1993); (Babbitt et al. in preparation).
- Operation of a network of 5 automatic weather stations and 4 sun photometers in Zambia (Study in progress).
- Comparison of dry versus humid savanna burning in Zambia (emissions and biomass consumption) (Ward et al. 1996); (Hao et al. 1996); (Shea et al. 1996).
- Study of fire emissions from active chitemene (shifting cultivation) and fallow chitemene sites in Zambia (Ward et al. in prep).
- Study of emissions from charcoal making in Zambia (Ward et al. in prep). Study of early dry-season fire emissions and biomass consumption in pure grasslands and open forest savanna sites in Zambia (Research completed August 1996).
- A study is planned for 1997 to measure the flux of smoke emitted from fires across the range of the humid-savanna ecosystems of northern Zambia. Our airborne sampling system (next section) and the network of sun photometers and automatic weather stations will be used for this study.

One example of important results from the FASS studies is the finding that emission production is normally linearly correlated with the fire-integrated combustion efficiency (CE) (Ward and Hardy 1991); (Ward and Radke 1993). CE is the percent of fuel carbon that is released as CO_2 and is sometimes approximated by "modified combustion efficiency" (MCE) ($\Delta CO_2/(\Delta CO_2 + \Delta CO)$), where the Δ refers to the measured fire

production of a gas above background levels. Flaming combustion has high CE and smoldering combustion has low CE. Thus, the fire-integrated CE (or MCE) is a useful index of the relative amount of flaming and smoldering that occurred over the course of the whole fire. The slope of the response function for emission production versus combustion efficiency is usually specific for each type of ecosystem. For example, in Figure 2 the x-axis is CE and the y-axis is CH_4 production in units of grams per kilogram of dry fuel. Each data point represents integrated data from a field fire. The points are divided into two groups; one from forest and one from grassland ecosystems. A line is fit to the data for each group, which is then a best fit model for CH_4 emission as a function of CE for that type of ecosystem. The vertical lines represent the typical or average CE we observe for various fire types. For example, savanna fires (solid lines) typically burn with a fire-integrated CE of 0.94 and produce about 2 g CH_4/kg, while primary forest fires (dashed lines) burn with lower CE and produce about 4 times as much CH_4 per unit amount of fuel.

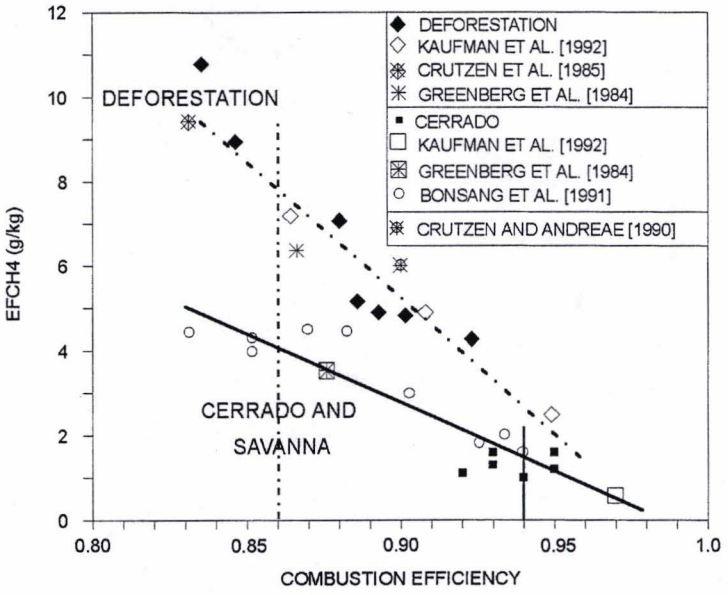

Figure 2. Methane production versus combustion efficiency shown for grass and deforestation fires (Ward et al. 1992).

Another example of FASS-derived results is that for savanna ecosystems of both southern Africa and Brazil, the fire-integrated combustion efficiency was found to be correlated with the mass ratio of standing dry grass to litter (Ward et al. 1996).

Combustion Laboratory

The United States Forest Service, Intermountain Fire Sciences Laboratory (IFSL), in Missoula, Montana, operates the world's largest controlled-environment, open, burning facility (Figure 3). Modeled fuel beds are burned with flame lengths up to 3-5 m on the continuously weighed platform.

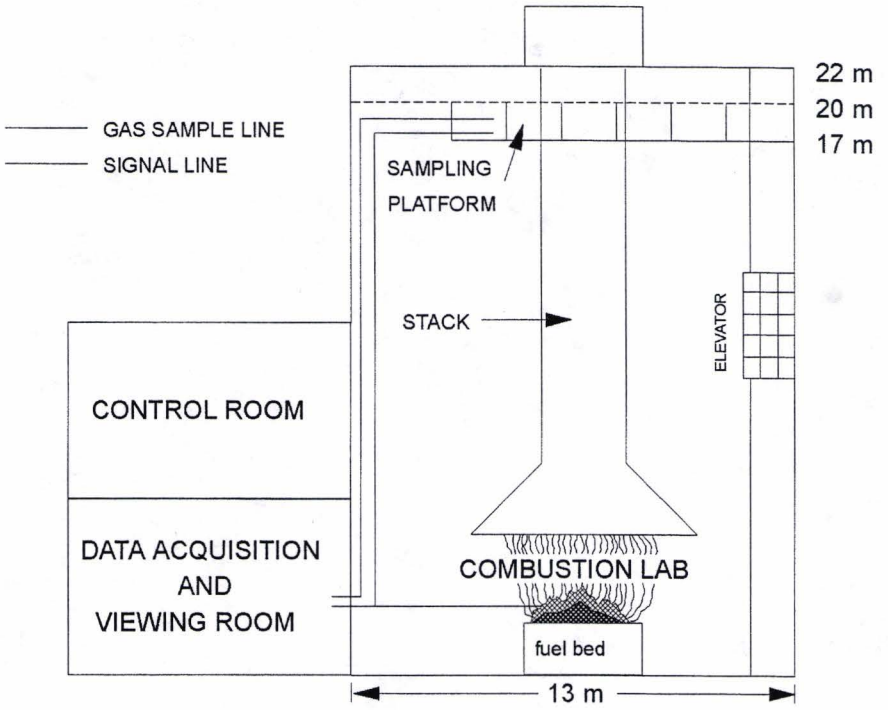

Figure 3. A diagram of the Intermountain Fire Sciences Laboratory combustion facility.

The emissions are funneled through a 1.6 m diameter flue outfitted with standard *and custom* stack-sampling methods (Finlayson-Pitts and Pitts 1986) including:

- A custom open-path Fourier transform infrared spectroscopy system (OP-FTIR) for real-time measurements of H_2O, CO_2, CO, (C_1 - C_3) hydrocarbons, aldehydes, alcohols, organic acids, nitric oxide, nitrogen dioxide, ammonia, hydrogen cyanide, carbonyl sulfide, and sulfur dioxide.
- Canister/Gas chromatography for integrated sampling of CO_2, CO, (C_1 - C_8) hydrocarbons, and halogenated hydrocarbons.
- Canister/Gas chromatography/Mass spectrometry for integrated sampling of CO_2, CO, hydrocarbons, and oxygenated organic compounds.
- Non-dispersive infrared absorption for real-time measurements of H_2O, CO_2, and CO.
- Chemiluminesence monitoring for real-time measurements of ozone, nitric oxide, and nitrogen dioxide.
- Filter collection and nephelometer for integrated and real-time particulate (PM2.5) production. Particulate is analyzed for elemental composition.

The laboratory measurement program allows discreet samples to be collected and analyzed sequentially during the life cycle of a fire. This has allowed us to produce quantitative, fuel-specific trace-gas emission factors for fires in a broad range of well-characterized biomass fuels (Yokelson et al. 1995b); (Yokelson et al. 1996a, b). In addition, these studies provide insight into important mechanisms of biomass combustion (Rothermel and Anderson 1966); (Yokelson et al. 1996a, b).

As noted above, the combustion laboratory has provided a platform for our pioneering use of OP-FTIR spectroscopic smoke composition measurements (Griffith et al. 1991);

(Yokelson et al. 1995a); (Yokelson et al. 1996a, b). In our spectroscopic, OP-FTIR measurements smoke samples are not collected; rather, IR energy is directed through the smoke. By analyzing the absorption of this energy as a function of frequency we can deduce the chemical composition of the smoke. Some advantages of this approach are:

- Reactive gases are not lost on the walls of sample lines and containers and can therefore be analyzed.
- The measurement is path-integrated and the path size can be varied to match the size of the smoke column, which reduces the potential uncertainty associated with point sampling.
- The measurements are continuous and in real-time so there is no uncertainty as to the proper time to sample, and dynamic processes can be followed.
- A wide range of species can be measured simultaneously.

Figure 4 shows portions of two OP-FTIR spectra acquired at different times during the same fire. The top trace was acquired while the fire was producing large amounts of white smoke from initial heating of the unburned fuel. The bottom trace was taken after the fuel was completely converted to glowing charcoal and there was no visible smoke, but the significant emissions indicated are still being produced. The spectra show a profound difference in the suite of gases emitted at the two different times by the different combustion processes. There are burning techniques that promote specific combustion processes and may allow some control over fire emissions. This example also illustrates the potential for different atmospheric impacts resulting from fires burning under various conditions.

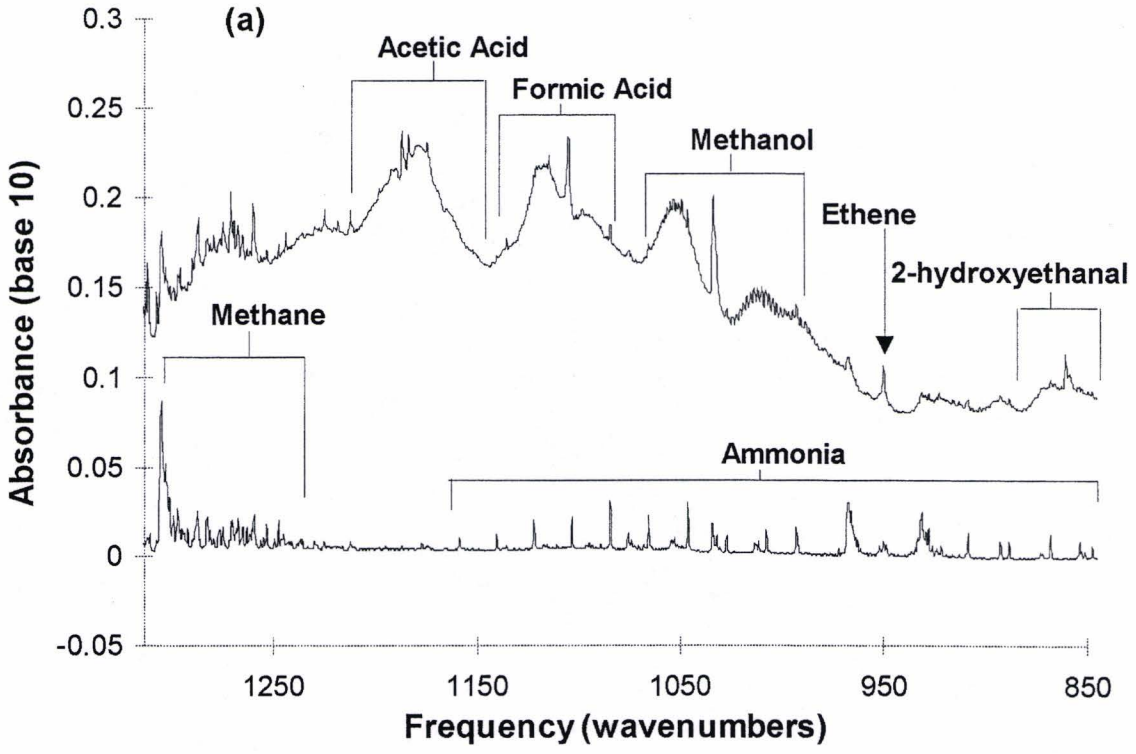

Figure 4. Sample OP-FTIR spectra acquired during a laboratory fire.

Also shown in Figure 4 is a significant peak due to 2-hydroxyethanal (glycolaldehyde), which was first discovered as a component of smoke in our work (Yokelson et al. 1996b). Finally, we further demonstrate that some of the anticipated advantages of the OP-FTIR technique were realized. Historically, nearly all previous emissions characterization has been by gas chromatography coupled to a flame ionization detector (GC/FID). In Figure 4 all the trace points above baseline are due to absorption by smoke components, but only the indicated peaks due to CH_4 and ethene (C_2H_4) are from compounds that can also be measured by GC/FID.

Figure 4 shows that many important smoke components, such as oxygenated organic compounds, were not measured by GC/FID. However, there were previous measurements of some of these compounds in smoke. Because the techniques used in these earlier measurements are subject to interference and sampling problems, it is important to compare those earlier measurements with our spectroscopic data. Figure 5 shows a typical example of such a comparison. Production of acetic acid in all published measurements is shown as a function of MCE (analogous to Figure 2). The OP-FTIR data, shown with dark squares in Figure 5, are well correlated with MCE. In contrast the other measurements are not correlated with MCE and are a factor of 10 to 1000 lower for important fire types. This is an important result because acetic acid reacts slowly with OH and will probably make a major contribution to precipitation acidity (Ayers et al. this volume). We have found similar, much higher emission levels for other compounds with important atmospheric effects and have begun exploring the implications of this using atmospheric plume chemistry models (Crutzen and Carmichael 1993).

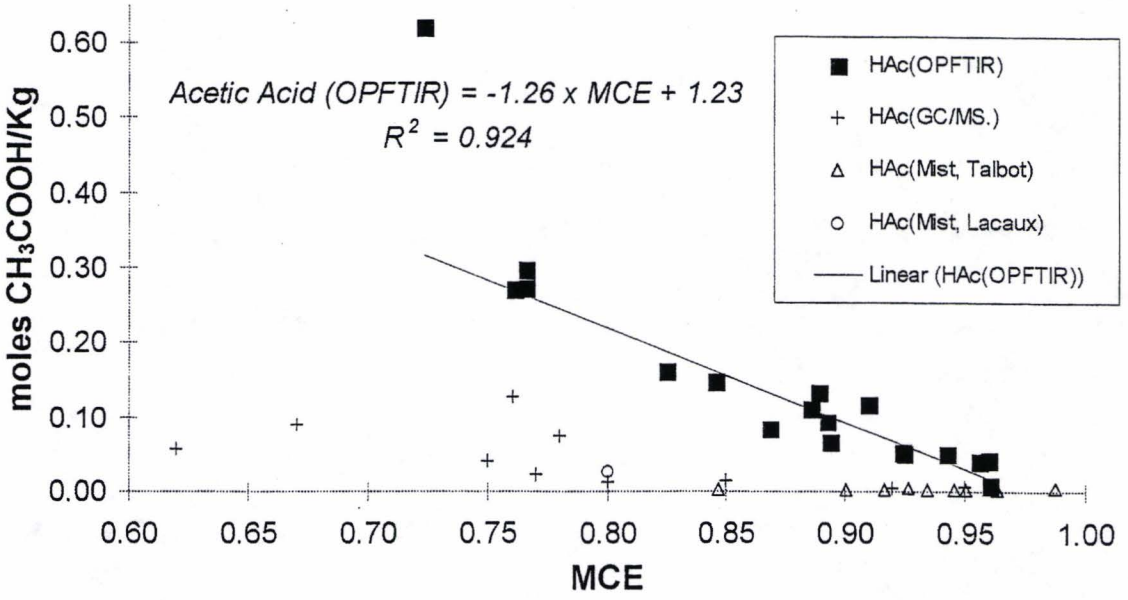

Figure 5. Comparison of published Acetic acid (HAc) measurements.

We now have extensive source strength data for many fuels and many compounds from our field and laboratory work. One small excerpt is shown in Table 1. We became

interested in measuring the emissions from smoldering organic soils after intensive study of Southeast Asian forestry issues. Table 1 shows what we think are the first detailed measurements of smoke composition from smoldering organic soils found in North America. An interesting discovery was that the nitrogen comes off primarily as ammonia (NH_3) from most organic soils, but with lower soil moisture content the nitrogen emissions are dominated by hydrogen cyanide (HCN).

Airborne Smoke Measurements

The rate of photochemical reactions that transform smoke constituents depends strongly on altitude and on smoke concentration (Chatfield et al. 1996). Validation of smoke plume atmospheric chemistry models will require extensive information acquired simultaneously on the position, composition, and dilution rates for the smoke. The dispersion (dilution, mixing, and transport) and transformation of smoke is best studied from aircraft. CO and particulate are good smoke tracers, and our IR and GC instruments can give detailed information on the chemical transformations.

Figure 6 shows the location of the "Chicken" and "Corral" Fires in central Idaho. On 9 September 1994, the Chicken Fire burned about 10,000 ha (on this day alone). Fires of this intensity can result from a lack of adequate fuel management. Millions of dollars (US) are spent suppressing a single fire of this type. The smoke column from the Chicken Fire rose > 6 km, crossed a major mountain range and then descended into the nearest downwind towns some 250 to 300 km distant. We were able to carry out airborne sampling at altitudes up to ~ 4 km (Babbitt et al. 1995). The smoke dispersion pattern and the flight plan are shown in Figure 6.

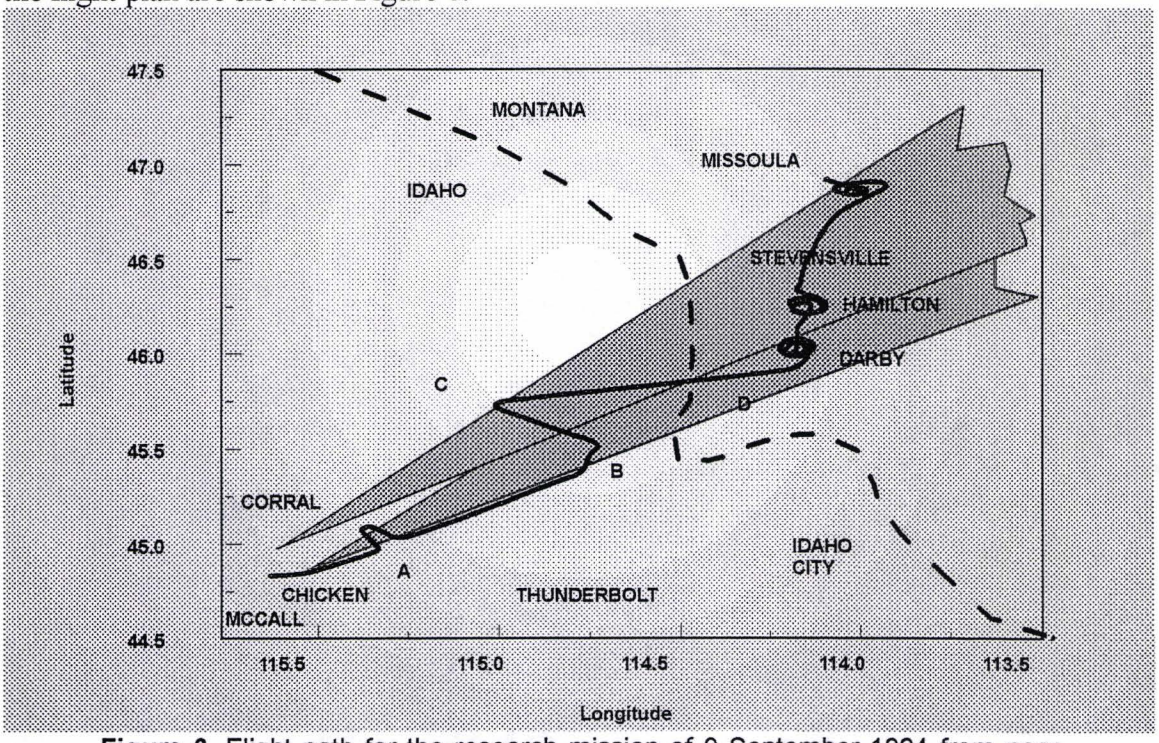

Figure 6. Flight path for the research mission of 9 September 1994 from near McCall, Idaho, to Missoula, Montana, crisscrossing plumes of the Chicken and Corral/Blackwell Fires (Babbitt et al. 1995).

In Figure 7 data from the flight are shown. The x-axis is time (in thousands of seconds) since the beginning of the flight, which is recorded by the GPS along with position. The thicker line shows the altitude and the thinner line indicates the particulate ($\mu g/m^3$) measured by nephelometry. The large capital letters cross-reference to the locations indicated on the map in Figure 6. Obviously, the highest concentrations are seen at "A" almost directly over the fire. Significant downwind impacts are seen in Darby (140 $\mu g/m^3$) and in Missoula (70 $\mu g/m^3$). These numbers can be compared with the new U. S. Environmental Protection Agency target standard of 50 $\mu g/m^3$. The likelihood of major smoke episodes in the future has increased as a result of past fire suppression practices. From the standpoint of atmospheric chemistry, this experiment shows the potential to measure the three-dimensional dispersion of the smoke.

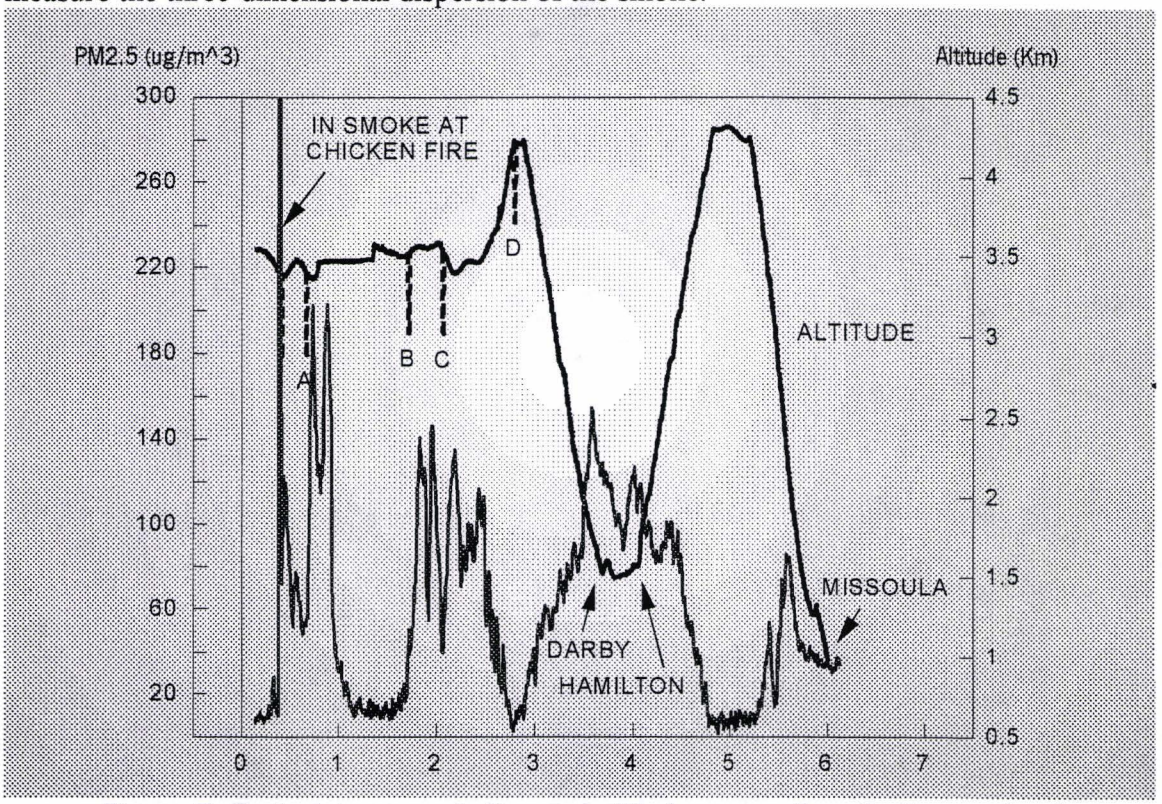

Figure 7. Particulate concentration and altitude versus time (in thousands of seconds) along the flight path shown in Figure 6 from McCall, ID, to Missoula, MT, on 9 September 1994.

The map in Figure 8 shows the location (10°S, 50°W) in Brazil of the "Racetrack Experiment" which was a joint project of our group and the National Aeronautics and Space Administration (NASA). The black square gives the horizontal coordinates for the flight path (100 km per side) of the ER2 (NASA research aircraft) which flew at ~ 20 km with infrared (IR) imaging equipment. The IR apparatus accurately maps the area of cerrado ecosystem burning in real time. To the east (upwind) there are no fires. The clean, upwind background air entrains the smoke from the racetrack region which rose from the burns and then "laid over" while moving downwind. We made horizontal transects at various altitudes in the clean upwind air first. Next, at two different times, once near noon when the fires were not yet intense and once late in the afternoon when the fires were at

peak intensity, we measured the CO_2 and CO throughout the plume. These data, coupled with the vertical wind profile, allow a rigorous calculation of the flux of carbon from the region for a given burned area. We can also use the CO_2/CO data to calculate the change in average combustion efficiency of the fires burning at the two different times. The CE's, used in models such as those illustrated in Figure 2 or 5, allow calculation of the temporally resolved regional flux for many other species.

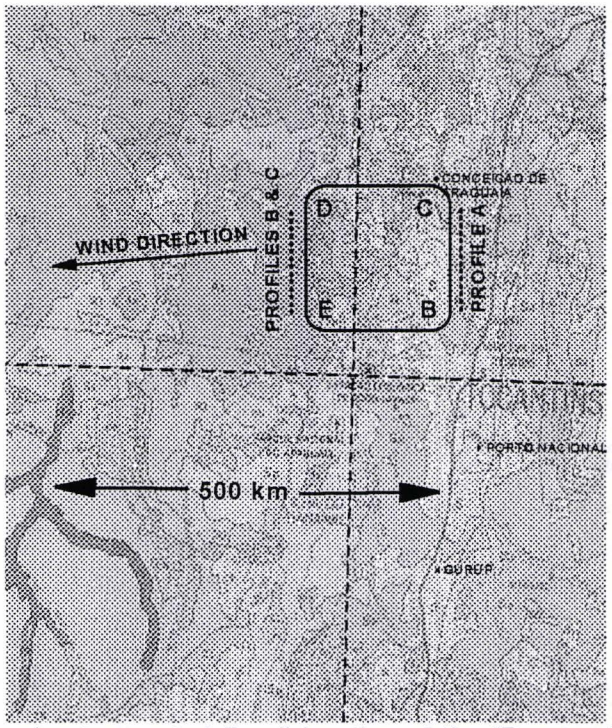

Figure 8. Map showing central Brazil location of the "Racetrack" Experiment. Dashed lines indicate 10°S and 50°W.

Other examples of our completed or future airborne studies include:

- In Brazil our airborne CO and particulate data contributed to identification of the prevailing transport mechanism that brings smoke over the Southern Atlantic.
- In the Brazilian state of Rondonia we have recently completed measurements of smoke from a pasture fire and two fires used to clear slashed, primary forest for agricultural purposes using our FASS and airborne sampling system simultaneously on the same fires (Babbitt et al. in preparation); (Ward et al. in preparation). (Babbitt et al. 1995)
- Future plans include airborne deployments of the FTIR (and other instrumentation) to enable simultaneous *in-situ* characterization of chemical transformations and transport.

Health Hazards of Smoke

In 1989, the Fire Chemistry Project participated in a national-level, detailed assessment of potential health effects associated with the exposure of wildland firefighters to smoke (Ward et al. 1989). A comprehensive study plan was developed and many studies have been conducted under its umbrella over the last several years. For example, firefighter

breathing-zone measurements of CO, formaldehyde, and particulate matter have been carried out in the field (Reinhardt et al. 1994), and firefighter lung capacity has been measured (Rothman et al. 1991). Recently, we have provided estimates for firefighter exposure to a large number of other compounds in smoke based on our measured emission ratios for these compounds to CO. For each compound, we have compared our exposure estimates to health and safety guidelines (McKenzie et al. 1995; Yokelson 1995a). Completion of the risk assessment will coincide with a major symposium on the topic scheduled for April 1997 in Missoula, Montana, U. S. A. We believe many of these results will be relevant to residents of communities exposed to smoke from wild and prescribed fires.

Future Activities and SEAFIRE

Biomass burning research in tropical America and Africa will undoubtedly assist in planning research in Southeast Asia. However, important differences must be recognized in vegetation (fuel), land-use, and other factors between Zambia, Brazil, and Southeast Asia (Seavoy 1973); (Kunstadter et al. 1978); (Whitmore 1985); (Riswan 1989); (Panayotou and Ashton 1992); (Pickford et al. 1992). Smoke transport across international boundaries, fuel-specific emissions data, special fire-use objectives, and other topics (all affecting air quality) need to be incorporated into a regional smoke management system for Southeast Asia. We hope to contribute in collaboration with scientists and managers from both Southeast Asia and other regions. An opportunity may exist under the umbrella of the Southeast Asian Fire Experiment (SEAFIRE) to expedite the needed research (Goldammer 1994).

Table 1. Average of all emission data for smoldering organic soils. Adapted from Yokelson et al. 1996b.

compound name	formula	100 X moles compound / total moles C detected	
carbon dioxide	CO_2	78.82	(3.593)
carbon monoxide	CO	17.10	(3.634)
methane	CH_4	1.220	(0.440)
ammonia	NH_3	0.932	(0.767)
acetic acid	CH_3COOH	0.306	(0.145)
hydrogen cyanide	HCN	0.292	(0.166)
methanol	CH_3OH	0.281	(0.100)
propene	C_3H_6	0.149	(0.027)
ethene	C_2H_4	0.140	(0.040)
formaldehyde	HCHO	0.132	(0.096)
phenol	C_6H_6O	0.107	(0.122)
formic acid	HCOOH	0.073	(0.060)
2-hydroxyethanal	$C_2H_4O_2$	0.032	(0.031)
carbonyl sulfide	OCS	0.021	(0.038)
ethyne	C_2H_2	0.013	(0.007)

The value of one standard deviation is given in parentheses.

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Fall 1995

Health Hazards of Smoke

USDA Forest Service — Missoula Technology & Development Center

The National Wildfire Coordinating Group coordinates wildland firefighting efforts among Federal and State agencies. The Coordinating Group assigned the Missoula Technology and Development Center (MTDC) to serve as the focal point for ongoing and future studies on the effects of wildland fire smoke on firefighters. This status report, the eleventh in a series, provides an update of project activities.

Project Review

The *Health Hazards of Smoke* project has included studies of smoke emissions, employee exposure, health effects, respiratory protection, and other risk management options. The next step is risk assessment, a process that integrates findings into risk calculations that will guide risk management decisions. Dr. Tom Booze, a toxicologist with the Radian Corporation will conduct the risk assessment, with advice and assistance from the project's technical committee. Dr. Booze met with the panel to outline the assessment process and to begin determining exposure levels, based on available data. A screening assessment will provide direction and determine gaps in the data base. A comprehensive risk assessment will follow. The risk assessment will help estimate the probable incidence of an adverse health effect to workers under various conditions, with a description of the uncertainties involved. Typical and reasonable maximum exposures (RME) will be determined for several categories of firefighters. Once the risks are known, managers will have the information needed to make informed decisions concerning the need for monitoring, tactics, training, medical surveillance, or respiratory protection.

Technical Committee

The *Health Hazards of Smoke* technical committee met from July 11 to 13 in Boise at the National Interagency Fire Center in conjunction with the meeting of the National Wildfire Coordinating Group's Safety and Health Working Team. Technical committee members attending included:

—Roger Ottmar, USDA Forest Service, Pacific Northwest Research Station

—Tim Reinhardt, Radian Corporation

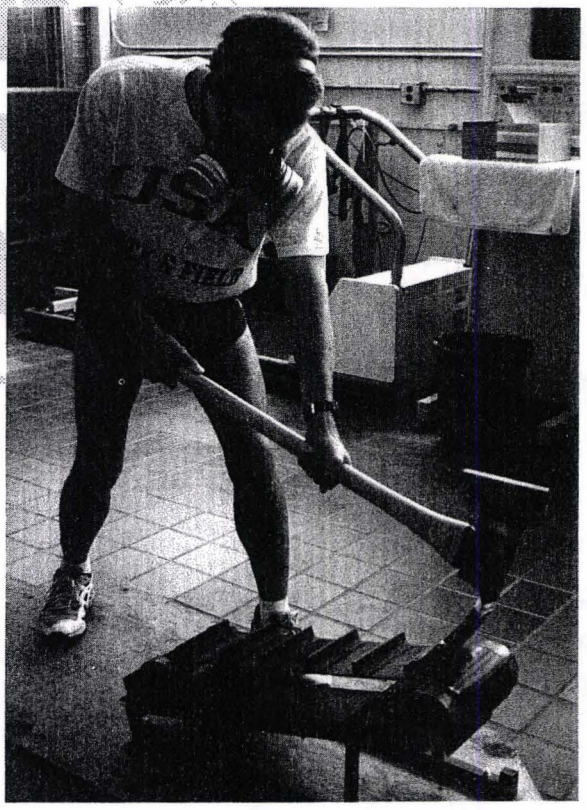
—Matt Silva, California Division of Forestry

—Wei Min Hao, USDA Forest Service, Intermountain Fire Sciences Laboratory

—Brian Olsen, USDI National Park Service

—Brian Sharkey, USDA Forest Service, MTDC.

The agenda included planning, reviews of projects, and discussion of program priorities. Considerable time was spent with Dr. Booze to begin work on the risk assessment procedure. The panel also began work on materials to communicate findings of the project with workers in the field. Following the meeting, program plans and priorities were reviewed with the Safety and Health Working Team.



Subject engages in a work test while wearing a respirator (see page 4).

Predictors ($p < 0.05$) of performance with an APR for combined (male and female) data included: strength (pull-ups, r = 0.77; push-ups, 0.85; upright row, 0.76; lat pull, 0.80), pulmonary function (FVC, 0.57; FEV1, 0.57), and the Pack Test (r = -0.68). Multiple regression analysis of fireline performance with an APR, as predicted by push-ups and the Pack Test, yielded r = 0.87. These results indicate that upper body work is not adversely affected by an APR at the levels of energy expenditure and ventilation found in this study. The ability to work with the APR can be predicted with measures of strength and/or performance on a job-related field test (Pack Test).

Firefighter Exposure to Air Toxics

R. Yokelson, Intermountain Fire Siences Laboratory (Interim Report) 1995.

Intermountain Fire Sciences Laboratory (IFSL) and University of Montana scientists have been using both established and new technology to estimate firefighter exposure levels for comparison with safety guidelines. A full assessment of this issue is complex for a number of reasons: the chemical composition of smoke is complex and the chemical analysis of smoke is difficult; exposure to smoke and the capacity to recover varies for individual firefighters; and there is great uncertainty for both the acute and chronic health effects of the smoke constituents acting individually or in concert.

Several types of studies have been conducted. An extensive study in the Pacific Northwest (Reinhardt et al., HHS Spring 1995) used personal dosimeters and sampled smoke in bags and on absorbent materials to measure firefighter exposure to carbon monoxide (CO) and some other air toxics. This is one of the few studies that have made measurements directly in the firefighters' breathing zone. A study at the University of Montana "froze" smoke from small laboratory-scale fires followed by Gas Chromatography/Mass Spectrometric (GC/MS) analysis. In a joint study by the IFSL and the Universities of Montana and Wollongong (Australia), a fourier transform infrared spectrometer (FTIR) was used to take optical spectra of the smoke from full-scale fires in the IFSL combustion laboratory.

The studies (one field, two lab) measured the average ratio of other air toxics to CO (T/CO) in smoke. The FTIR study looked at the changing chemical composition of smoke in real time, which allows an assessment of possible peak exposure levels. The results of the field study give an average and maximum firefighter exposure to CO that is well below occupational exposure guidelines. Combining the results of the studies allows us to compute long-term exposure to other chemicals from the formula: FET = FECO x T/CO (where FET stands for firefighter exposure to toxin and FECO stands for firefighter exposure to CO). Examples of measurements of T/CO are shown in Table 2, where +/- signs indicate the precision of the measurement in that study. In these examples the FTIR measurement of T/CO is about twice as large as the other measurement. This indicates that the uncertainty in this ratio is about a factor of 2, which is not large compared to the real differences between various types of smoke or the much greater uncertainties in determining a "safe" exposure level.

Using this type of analysis, the average exposure to toxic gases other than CO is also well below occupational guidelines.

Peak Exposures—To complete a risk assessment, we must determine appropriate conditions for measuring Reasonable Maximum Exposure (RME) levels. The peak exposures measured in the field study were well below current occupational guidelines. However, there is a basis for concern because some of the nine fires in the FTIR study showed much higher peak levels than were observed in the field. The highest peak levels are from FTIR measurements made in the smoke 18.3 m (60 ft) above a fire burning with 0.3 to 0.91 meter (1 to 3 ft) flames in green pine needles. The smoke temperature was 153°F with visibility under 1 m. Table 2 shows some of these results and an example of how these measurements can be used to perform preliminary screening of the smoke constituents to determine which are of the most concern for potential health effects. In Table 3 the maximum value of the data points (measured at 1-min intervals) are compared to

Table 2—Intercomparison of measurements of average T/CO.

Toxics/CO ratio	GC/MS (lab)	Field	FTIR (lab)
Formaldehyde/CO	(no data)	0.008 +/- 0.00024	0.021 +/- 0.01
Methanol/CO	0.011 +/- 0.009	(no data)	0.023 +/- 0.01

Table 3—Peak exposures for firefighters compared to safety standards.

Chemical	Maximum	IDLH	Max/IDLH	OSHA peak
CO	587 ppm	1500 ppm	0.4	200 ppm*
Formaldehyde	25	30	0.83	2
Methanol	28	25,000	0.001	-

*Ceiling—not to be exceeded.

the Immediately Dangerous to Life and Health (IDLH) limits set by NIOSH, and the peak exposure limit (10 to 15 min) set by OSHA.

The results of this type of analysis suggest that of the 16 compounds measured in real time in smoke in the FTIR study, formaldehyde may be of the most concern. These are early laboratory results that have not been verified in the field.

Future Research—To complete the risk assessment for firefighters, a number of activities will improve the accuracy of the assessment, including: careful consideration to the appropriate conditions for measuring RME's; deploying at least one more instrumental technique to measure FECO in the field (e.g., using the FTIR near a crew); and reducing uncertainty in T/CO by comparing instruments in the same smoke (e.g., the dosimeter and GC/MS simultaneously with the FTIR in the laboratory, or the dosimeter with the FTIR in the field).

Risk Assessment

Risk Assessment: Wildland Firefighters

Booze, T.

This study involves a health risk assessment for wildland firefighters exposed to smoke from wildland fires or prescribed burns. The objective is to provide the technical information needed to help support risk management decisions to protect wildland firefighters against smoke exposure. The first task is the hazard assessment, identifying the chemicals and physical agents to be addressed in the risk assessment, and identifying the toxicological endpoints of concern. We have currently identified formaldehyde, acrolein, polynuclear aromatic hydrocarbons (PAH's), carbon monoxide, and benzene as chemicals to evaluate. These chemicals were chosen based on previous laboratory and field studies.

The next step is the dose-response assessment, where the appropriate toxicity factors are identified for each chemical. These generally include cancer slope factors, reference doses, and standards with which acute (short-term) exposures are compared. Although many toxicity factors are available, the values may be for adverse effects unrelated to smoke exposure. In these cases toxicity values may need to be developed for effects of interest. The third step is the exposure assessment, where the types of exposures to be evaluated are decided upon. This includes job categories, fuel types, types of fire exposure, exposure frequency, and exposure duration. We have included hand crews and engine crews as two general job categories and have estimated exposure frequency for both typical and reasonable maximum exposures (RME). The concentrations of chemicals in smoke used in this assessment are based on previous field studies.

The final step in the risk assessment is the risk characterization, where exposure estimates are combined with dose-response data to estimate the potential health risk for various job categories and exposures.

—Tom Booze, Ph.D., is a toxicologist associated with the Radian Corporation. He is experienced in wildland firefighting, and worked as a member of the Mendocino Hot Shots.

Particulate Standard

The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed a new threshold limit value (TLV) for particulates not otherwise classified (PNOC). In contrast to fibrinogenic dusts, which cause scar tissue in the lungs, so called "nuisance dusts" show little adverse impact on lungs. Nor do they produce significant organic disease or toxic effects when exposures are kept under reasonable control. The PNOC's do not alter air spaces or form collagen to a significant extent, and tissue reactions are potentially reversible. The PNOC TLV is based not on chemical toxicity, but on physical overloading clearance mechanisms of the respiratory tract's.

Recent animal and human studies indicate that exposure to excessive amounts of dust can cause adverse health effects. Particulate overload causes reactions that can stimulate fibrosis. Alveolar macrophages can become sequestration compartments. As dust concentration increases in the lung the retention time increases. Physical overload may lead to chemical toxicity such as pulmonary alveolar proteinosis. For these reasons, the ACGIH proposes lowering the TLV for PNOC to 3 mg/m^3 for respirable particulate containing no asbestos and < 1% crystalline silica.

The ACGIH believes that the lung's clearance mechanisms must continue to be functional. They recommend the 3 mg/m^3 standard to minimize the potential for compromised pulmonary clearance. The current Occupational Safety and Health Administration's permissible exposure limit (PEL) for respirable particulate is 5 mg/m^3. The ACGIH rationale for a lower standard is that the OSHA PEL was developed in 1969 to prevent physical irritation to the worker. The proposed TLV is based on toxicological data involving pulmonary overload of macrophages. The new limit is based on minimizing the potential for loss of pulmonary clearance mechanisms.

Both the ACGIH TLV and the OSHA PEL describe the time-weighted average (TWA) concentration of a normal 8-hr workday, to which nearly all workers may be

Spring 1996

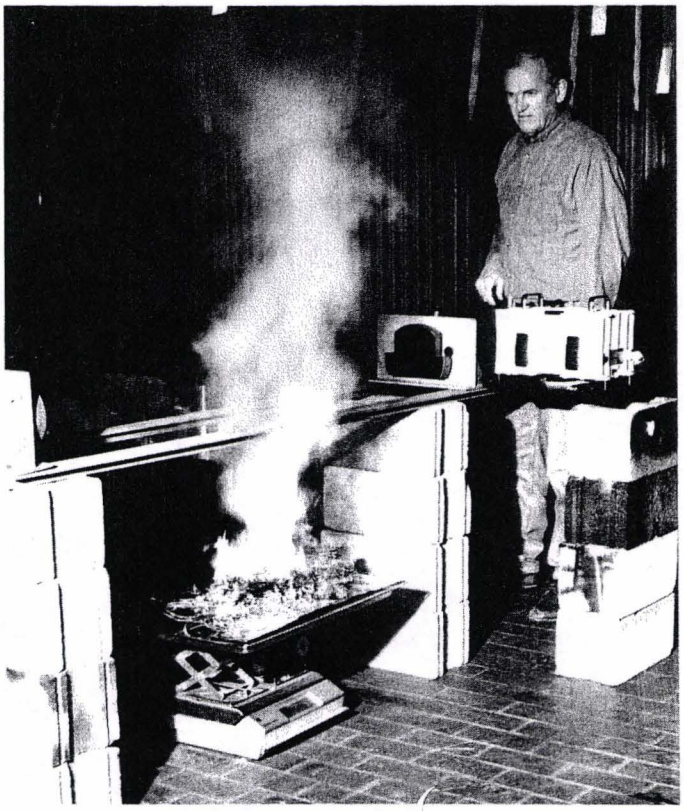
Health Hazards of Smoke

USDA Forest Service — Missoula Technology & Development Center

The National Wildfire Coordinating Group coordinates wildland firefighting efforts among Federal and State agencies. The Coordinating Group assigned the Missoula Technology and Development Center to serve as the focal point for ongoing and future studies on the effects of wildland fire smoke on firefighters. This status report, the twelfth in the series, provides a review of project activities.

Project Review

Throughout the history of wildland fire suppression, firefighters have been exposed to smoke. The smoke has been viewed as a health, esthetic, economic, or political problem for communities and agencies. Until recently, little concern was expressed for the health of those most exposed to the problem, wildland firefighters. In his history of fire in America (1982), Pyne alludes to an emerging interest in carbon monoxide as a problem for firefighters. In the 1960's, researchers began probing the effects of working for days and weeks in the forest fire environment, but this research was episodic and the results were inconclusive (Thoele, 1995). A 1985 Fire Equipment Working Team survey found that dealing with smoke and carbon monoxide was not a high priority for fire managers. That position changed dramatically with the 1987 and 1988 fire seasons, when thousands of firefighters lined up at medical tents with respiratory complaints. To address the problem the National Wildfire Coordinating Group (NWCG), related agencies, employee groups, and specialists in occupational medicine, industrial hygiene, and risk management met early in 1989 to outline a study plan for determining the immediate and long-term exposure to forest fire smoke (Ward, Rothman, and Strickland, 1989).



Ron Susott of the fire chemistry project monitors a test using a new spectrometer. The smoke from a small-scale fire passes through an infrared beam that is reflected back to the FTIR for analysis (see report on page 3).

The comprehensive plan proposed studies in the areas of: emissions characterization, employee exposure, health effects, risk assessment, and risk management. The NWCG assigned the Missoula Technology and Development Center (MTDC) to serve as the focal point for ongoing and future studies on the effects of wildland fire smoke on firefighters. The Center convened a technical panel to help guide the project, to review and evaluate existing research, and to identify research and funding priorities. The Center publishes a semiannual report to communicate recent research and future directions of the Health Hazards of Smoke project to firefighters, fire managers, researchers, regulatory agencies, organizations, and manufacturers.

Smoke Studies

The Fire Chemistry Project at the Intermountain Fire Sciences Laboratory has installed new instrumentation to characterize the chemical composition of smoke. The instrument is an open-path Fourier transform infrared spectrometer (FTIR) that allows real-time analysis without the need to collect samples. The instrument has already been used to measure emissions from many fuel types including: ponderosa pine, sagebrush, grasses, poplar, maple leaves, and a variety of organic soils. The higher sensitivity and rapid response of the new instrument make it possible to survey a wide variety of fuels and to correlate fire behavior with emissions. For example, the white smoke generated by rapid heating of fresh fuel contains many oxygenated compounds not detected in the emissions from glowing combustion, and a higher ratio of formaldehyde (**Figure 1**). White smoke also contained a sugar that had not been detected in smoke before. Larger fuel elements were found to smolder in a way that produces a larger ratio of white smoke to glowing combustion.

The new system also has high resistance to chemical interference that plagues measurements of many chemicals, including acrolein. Acrolein has not yet been detected in the emissions from any of the samples, suggesting that firefighter exposure to acrolein may be lower than previous estimates based on field studies. Extensive investigation of how fuels and fire behavior affect emissions could produce guidelines to help firefighters reduce their exposure to the health hazards of smoke. (A description of the FTIR can be found in Health Hazards of Smoke, No. 8, Spring 1994: results from a prototype of this instrument, borrowed from the National Center for Atmospheric Research, were featured in Health Hazards of Smoke, No. 11, Fall 1995. For information on the Fire Chemistry Project contact Darold Ward, Ph.D., at the Intermountain Fire Sciences Laboratory in Missoula, MT.).

(**Note:** *Acrolein has been detected in all employee exposure studies. It has been found to be a significant contributor to the noncancer hazard index.* *See Risk Assessment on page 5.*)

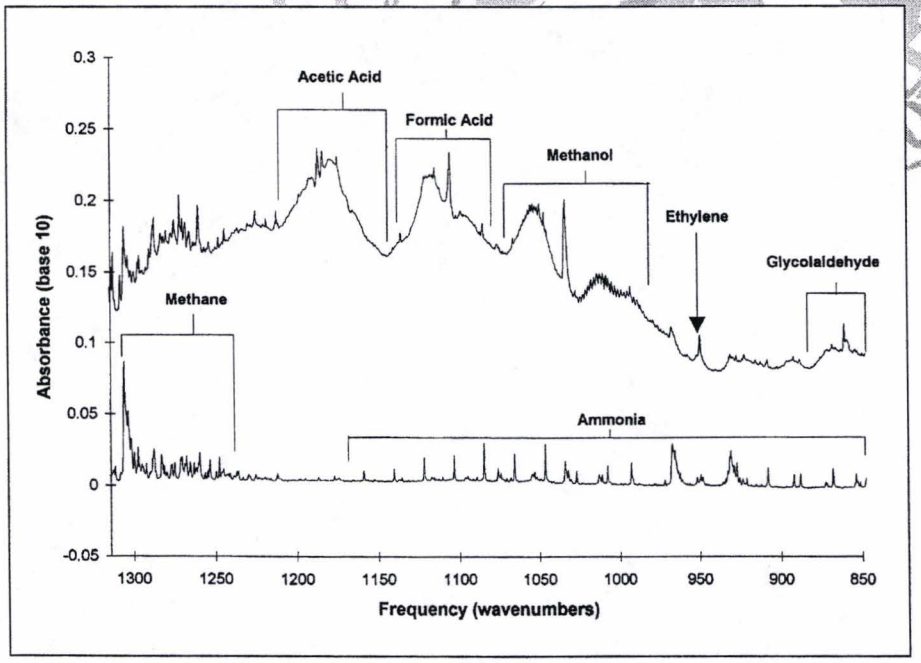


Figure 1—A portion of the spectrum of white smoke (top) shows many oxygenated compounds, while the same spectral region for glowing emissions (bottom) shows only ammonia and methane.

Research

Evaluation of Full-Face Air-Purifying Respirators for Wildland Firefighting Use
Beason, D., Johnson, J., Foote, K., and Weaver, W. Lawrence Livermore National Laboratory and California Department of Forestry and Fire Protection, Summary Report, 1996.

Wildland fire suppression personnel employed by the California Department of Forestry do not currently have equipment to protect themselves from the short-term (acute) effects of smoke from wildland fires. In addition, no regulations exist that specify appropriate respiratory protection. The current air-purifying respirator technology and carbon monoxide monitoring have not been adapted to fit wildland fire suppression requirements. This 3-year limited study evaluated the ability of wildland firefighters to perform their normal job function while wearing full-face air-purifying respirators.

In the first 2 years of this study a prototype "smart" air-purifying respirator that incorporated a real-time carbon monoxide monitor into a commercial full-face respirator was designed, developed, and field tested. Data on carbon monoxide exposure while fighting wildland fires was collected. During the third year of this study eight different commercially available full-face air-purifying respirators equipped with a variety of cartridges were evaluated. An apparatus to help the firefighter carry the respirator and carbon monoxide personal monitor was designed and fabricated. A smoke exposure test method was developed and a laboratory study on the penetration of smoke through respirator cartridges was conducted.

The authors concluded that the full-face air-purifying respirator was well received by firefighters;

Smoke chemistry measurements by airborne Fourier transform infrared spectroscopy (AFTIR).

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Introduction

There are several important advantages to measuring trace gas emissions from biomass fires by Fourier transform infrared spectroscopy (FTIR). These include:

1. The measurement provides simultaneous quantification of a wide variety of reactive and stable gases (including all the major gases) with low interference between species.
2. The measurement is continuous to allow investigation of dynamic processes and reduce the uncertainty associated with grab sampling or, alternatively, the measurement is repetitive or time-integrated for the latter purpose.
3. The spatial scale of the measurement can be made similar to the size of the phenomenon being investigated to reduce uncertainty associated with fixed-point sampling.
4. There is high potential to observe and identify unanticipated species.

Modern Fourier transform infrared spectrometers (FTIR) can measure the entire mid-IR (400 - 4000 cm^{-1}) spectrum of a gas sample in under one second with sufficient sensitivity to provide typical detection limits in the low ppb range. In a series of detailed, FTIR-based *laboratory* studies we have characterized the temporal behavior and wide variety of initial fire emissions. We have shown that a large percentage of the initial emissions are reactive and therefore difficult to analyze by traditional measurement techniques requiring extended sample storage. We have found oxygenated organic compounds, in general, present at levels 10 to 1000 times those measured in many previous studies. One oxygenated compound in particular, 2-hydroxyethanal, was identified for the first time as a smoke component and accounted for up to one percent of the fuel carbon loss (about twice the typical CH_4 emission factor). Thus these compounds may serve as an important, but previously overlooked, source of radicals in the initial smoke plume. Our spectra also indicate that high levels of terpenes could be ubiquitous in initial biomass burning plumes. We have been unable to confirm these results by GC/FID or GC/MS, possibly because these species are lost during sampling or analysis. Smoke storage experiments in our glass multipass cell show stable levels of CO_2, CO, CH_4, and C_2 hydrocarbons while the "terpene" signal decays within a few hours.

Most of the trace gases identified in biomass burning studies, (with the notable exception of CO_2 and CH_4) react too quickly in the atmosphere to be well-mixed in the global troposphere. Local-regional processing will transform the initial smoke and strongly affect the ultimate global impact. For example the smoke dilution rate and smoke altitude (temperature) will strongly influence the reaction rates and absorption cross-sections of many of the smoke constituents. The early atmospheric processing of fire emissions, in general, remains poorly understood.

Previous airborne measurements of biomass fires have emphasized sampling of haze layers covering large geographic areas where many fires burn simultaneously. Thus, comparison of smoke processing models to field data sets has required that the smoke age in individual samples had to be calculated (or guessed) based on certain observed chemical ratios assumed to be photochemically controlled. During NH spring and summer of

1997, the Forest Service and the University of Montana collaborated in a preliminary effort to acquire field measurements of smoke composition, from aircraft, well-suited for *direct* comparison to models of the chemistry in biomass burning plumes. The measurements were conducted aboard the Forest Service King Air B-90 in North Carolina and Alaska on large, isolated plumes both near the source and as far downwind as the aircraft range or fire size allowed. As part of this effort, a new type of airborne smoke-sampling system consisting of a Fourier transform infrared spectrometer coupled to a "flow-through" multipass cell (AFTIR) was designed and deployed for the first time.

Experimental

The King Air can support a scientific payload, including passengers, of approximately 800 kg for a three hour flight time. To enable the most possible instrumentation for smoke plume characterization a primary design consideration for AFTIR was minimizing size and weight while maximizing the optical path length (proportional to sensitivity). Figure 1 shows a photo of the AFTIR system which is described in detail below.

Optical System Design

The IR beam exiting the spectrometer (MIDAC Inc.) is steered by appropriate transfer optics to a "tripled" white cell (IR Analysis, Inc.) featuring coated silver mirrors and retroreflectors mounted inside a 15 (i.d.) X 91 cm Pyrex tube. The variable path cell has a base path of 0.81 m and was passed 120 times for a total path of 97.5 m. Viton O-rings seal the ends of the tube to nickel-plated aluminum endplates. Temperature is measured by internal thermocouples at both ends of the cell while pressure is measured by a manometer at the aft end only. All metal surfaces inside the cell were coated with halocarbon wax to reduce surface reactivity as much as possible. The exit beam from the cell is directed by mirrors and a ZnSe lens onto the LN_2 cooled wideband MCT detector (Graseby, Inc.). The above optical elements of the AFTIR system are co-mounted on a rigid 28 x 175 x 11 cm honeycomb core optical table (Newport, Inc.) which was shock mounted to the seat tracks of the King Air using a combination of rubber pads and cable type shock mounts (Aeroflex, Inc.) for vibration isolation. Total system weight including a protective sheet metal shield was approximately 64 kg.

Sample/Flow System

An aluminum plate was built to temporarily replace the copilots window upon which forward-facing aluminum elbows were mounted to serve as sample inlets. The AFTIR inlet was 2.5 cm i.d. and was wax-coated as described above. Approximately 1.5 m of 1" i.d. teflon tubing connected the aircraft sample inlet to the multipass cell inlet located near the top of the front endplate. A deflector attached to the inside of the front endplate served to deflect the incoming gas stream into a circular pattern behind the field mirror. The gas then flowed slowly through large notches in the field mirror and through the cell to an outlet near the bottom of the back endplate. Air/solenoid actuated, 5 cm i.d. butterfly valves (wax-coated) provide flow control for the inlet and outlet line. These valves can be controlled manually for plume penetrations or cycled by the system computer for automated sampling. Use of the valves allowed us to perform insitu measurements of the cell exchange time by opening the valves in clean air after "grabbing" a sample in a smoke plume. The 1/e exchange time was typically 7-8 s (considerably longer than the 1.7 s spectrometer scan speed) and limited our spatial accuracy to ca. 800 m at the King Air cruising speed of 90 ms^{-1}. No on-line calibration standards were measured during our initial deployments, but comparisons were made with independent measurements of CO by a TEACO NDIR CO which had nearly identical time response.

Data acquisition protocols

Three data acquisition modes were utilized. Initially, spectra were collected continuously during flight using ram pressure to drive air (or smoke) through the cell. It was

quickly discovered that many of the plume penetrations were on a time scale similar to the cell exchange rate *and* that the single-scan noise level in the important 900-1100 cm^{-1} region was enormously reduced when *both* the inlet and outlet valves were closed. (This may have been due to elimination of propeller-induced pressure fluctuations.) Furthermore, a storage test of concentrated smoke in the cell showed that all the identified species except formic acid and 2-hydroxyethanal were stable for at least 5 minutes. Thus, the continuous measurements were soon superseded by one of two intermittent sampling protocols.

For near-source plume penetrations both valves were initially open and then were simultaneously closed just before exiting the plume when the cell should have been well-flushed with smoke. The valves remained closed for several minutes while spectra of the smoke sample were coadded to improve S:N. Only the first few spectra would be used for measurement of less stable species. Next, both valves were opened and the cell was flushed with clean air. After ca. 30 - 60 s both valves were closed again and spectra were coadded for a "background" scan. This last step typically took place while turning the plane in preparation for another plume penetration. For long-axis plume profiles the valves were programmed for a continuous (1 min open: 2 min closed) cycle.

Other simultaneous measurements

Other measurements made on each King Air flight included: CO_2 and H_2O (Licor model Li6262); CO (TEACO model 48); NO (TEACO model 42); O_3 (TEACO model 560); GPS (Magnavox, then Garmin 12XL); smoke absorption (Radiance Research); and particulate concentration (Radiance Research nephelometer M903). Data from each of these instruments was recorded every second. In addition, each flight carried 30 - 50 stainless steel canisters and one large Tedlar bag (which could be filled within ca. 10 s at selected locations). Teflon filter samples were drawn from the bag or ambient air. A sonde (Avtech, Inc.) for T, RH, lat, long, alt, and 3D winds was mounted on a Cessna 172 which flew a similar flight path to the King Air as closely as possible in time. The sonde readings were recorded every second.

Results

A typical 3 hour flight produced ca. 7200 FTIR spectra and 18 channels of complementary information with a 1 s time base. Only preliminary, "peak-height based" analysis of a few spectra are presented here.

Initial inspection of spectra, acquired within a few kilometers of the fires, showed strong, readily analyzed, signals for at least 9 species including: H_2O, CO_2, CO, CH_4, H_2CO, CH_3COOH, CH_3OH, C_2H_4, and NH_3. The first flight probed smoke from a controlled burn in a hurricane-damaged forest located within Camp Lejeune. Cursory analysis of a typical smoke spectrum from this flight yielded excess smoke concentrations including 3.64 ppm CO, .29 ppm CH_4, and .11 ppm H_2CO. On a later flight which sampled smoke from a small wildfire near Goldsboro North Carolina we acquired spectra with the valves closed as described above. Preliminary analysis of a spectrum from this flight yielded excess smoke concentrations of 2.5 ppm CO, 62 ppb CH_3OH, 48 ppb NH_3, 37 ppb CH_3COOH, and 29 ppb C_2H_4 (partially seen in Figure 2). The estimated detection level for these compounds was typically around 5 - 10 ppb. Most of the compounds detected are much rarer in background air than in smoke. Thus, the measured ratio of these compounds to CO, or to each other, should quite accurately reflect smoke composition. Initial inspection of the data from the complementary instruments indicates that all of these were working well on the early flights with the exception of the smoke absorption and O_3 instrument.

Discussion/Conclusions

Comparison to other measurements

The CH_4/CO ratio of 0.08 and the C_2H_4/CO ratio of 0.012 are very near average literature values for these compounds. For instance, Lobert et al quote 0.0911 and 0.0121 respectively. We observed a H_2CO/CO value

of 0.03 which is a little higher than most of the literature *average* values which agree within a factor of 2. For example, in our most detailed laboratory study, we measure 0.0210 ± 0.0151 (1σ, n = 93) with the higher values being due to hardwood fuels. Literature results for other "light" oxygenated organic compounds show more variation as discussed earlier. Recently, Worden et al reported values for four trace gas emissions from two biomass fires measured with an airborne (spectral) emission spectrometer. They observed values for CH_3OH/CO of 0.046 and 0.016. Our preliminary airborne observation of 0.031 is within that range. Most literature reports for CH_3COOH/CO fall well below our recent laboratory value of 0.0212 ± 0.0145 (1σ, n = 92). In contrast, our first airborne observation of 0.015 is in good agreement with all of our laboratory studies.

Conclusions

These data initially provide a significant field verification of the high concentrations for a *suite* of oxygenated organic compounds previously observed in our laboratory fires. The results of a growing body of spectroscopic fire studies suggest that oxygenated organic compounds deserve more attention in modeling the atmospheric influence of fires.

Smoke composition measurements made by other techniques suggest that HNO_3, H_2O_2, PAN, O_3 and other photochemically produced species will be present at measurable levels in our AFTIR spectra acquired further downwind. Our real-time instruments, and canister samples should also provide information on changes in the chemical composition of the smoke. The plume chemistry must depend strongly on the dispersion pattern of the smoke which was well-mapped by monitoring CO and particulate. When our database on the chemical composition and dilution of the smoke is complete, it will be coupled with estimates of the atmospheric processing time for the smoke samples based on the 3D wind data.

Figures

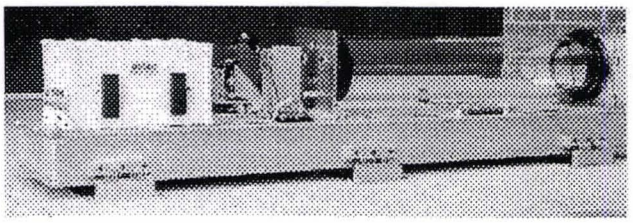

Figure 1. The photo shows the AFTIR system (minus the sample lines and computer) flown on the Forest Service King Air B-90 to sample smoke from biomass fires during April 1997. The major components seen are the shock mounted optical table, FTIR, custom transfer optics, a "tripled" white (multipass) cell, and external detector.

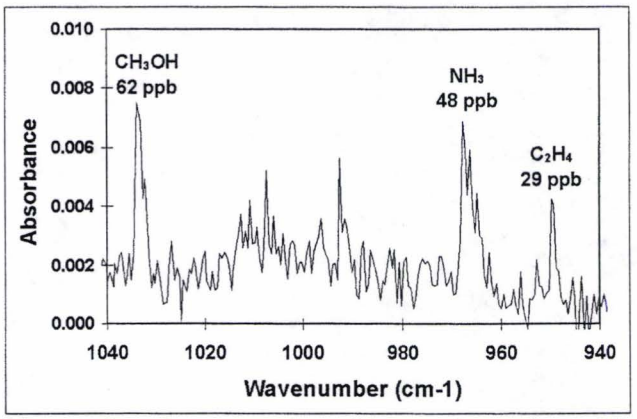

Figure 2. An example of a portion of an IR smoke spectrum obtained in our initial AFTIR deployment is shown with some of the larger peaks labeled. Preliminary analysis of our spectra shows several oxygenated organics (H_2CO, CH_3COOH, and CH_3OH) emitted at ~ 2% of the CO which is in good agreement with our lab studies.

Trace Gas Emissions from Specific Biomass Fire-types

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Abstract

The Land-Use Change and Forestry chapter of the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* recognizes biomass fires as an important source of greenhouse gases and other trace gases. The guidelines also suggest that it may be appropriate to use different trace gas emission factors for different types of fires. However, currently, a single set of "default" emission factors is given which is intended for application to all on-site biomass burning. We have been using a simple, preliminary classification scheme for tropical fire-types and a straightforward model for predicting emission factors as a function of fire-type for estimating emissions from biomass burning (Ward et al 1992). Use of this system results in a CH_4 emission factor ($EFCH_4$) from primary forest deforestation burns which is four times larger than $EFCH_4$ from savanna fires *per unit mass of fuel*. In general, adjusting emission factors for fire-type should improve trace gas inventories; even when only rudimentary knowledge is available regarding the distribution of fire-types occurring in a region. In this paper, the use of this system (and related systems) is referenced, described, or developed for a number of atmospherically significant, biomass fire emissions. This approach could be used by national level experts, together with the best information on the fire-types occurring in their countries, to develop more accurate alternatives to the IPCC default values.

Introduction

Fires transform biomass into many different products. Trace gases and aerosols are injected into the atmosphere while charcoal and tar remain on site. Large quantities of ash also result; of which a significant fraction is usually redistributed by wind or rain (Raison et al 1985). The combustion processes leading to these products have been discussed elsewhere (Yokelson et al 1996b; Yokelson et al 1997a). A summary is given here. Initial heating of unburned fuel releases the more volatile components by distillation and produces oxygenated organic compounds by depolymermization and bond breaking. The residual solid is known as low temperature char and has high aliphatic content. Continued temperature increase releases hydrocarbon gases resulting in high temperature char (with high aromatic content). Glowing combustion on the surface of char releases CO_2 and CO and other gases. A small fraction of the gases, especially the higher molecular weight compounds, may recondense into "tar." A somewhat larger fraction of the gases escape into the atmosphere without being oxidized in flames and are known as smoldering products. Normally, most of the initially produced gases undergo further oxidation in flames resulting in CO_2, H_2O, NO, SO_2 and other flaming products. Aerosols are made by

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a variety of less well-understood processes. The residual, on-site, solid products are primarily found as char, which is enriched in carbon, or as ash, which is high in inorganic content. The relative production of the flaming and smoldering compounds is affected by many variables (Ward et al 1996). Fine, dry, or loosely packed fuels tend to be consumed by flaming combustion while large, wet or densely packed fuels tend to be consumed by smoldering combustion. Other variables affecting the mix of flaming and smoldering include weather (such as wind, rain, temperature, and RH) or the burning (slashing and ignition) techniques (Seavoy 1973; Kunstadter et al 1978; Kauffman and Uhl 1990).

Several useful parameters have been developed which indicate the relative amount of flaming and smoldering combustion in a fire. These parameters are computed from fire-integrated measurements of the emissions as discussed by Ward and Radke (1993). These parameters and their definitions include:

1. Combustion efficiency (CE) which is defined as the fraction of fuel carbon burned released as CO_2.
2. Modified combustion efficiency (MCE) defined as $(\Delta CO_2/(\Delta CO_2 + \Delta CO))$.
3. CO/CO_2 ratio defined as $\Delta CO/ \Delta CO_2$.

In these definitions, "Δ" refers to the measured fire production of a gas above background levels. CE requires the most data to compute while MCE and CO/CO_2 require the measurement of only two gases. MCE has the further advantage that it is highly correlated with CE (Ward and Radke 1993). The methodology used to measure carbonaceous products varies among studies and the mathematical form of MCE is not identical to the CO/CO_2 ratio. However, the important point is that proper use of any of these parameters can illustrate the different fire-integrated combustion characteristics that result from different fire-types. Flaming combustion has high CE, even higher MCE, and a low CO/CO_2 ratio. Smoldering combustion has lower CE and MCE than flaming, but a higher CO/CO_2 ratio. Thus, the fire-integrated CE, MCE, or CO/CO_2 ratio is a useful index of the relative amount of flaming and smoldering that occurred over the course of the whole fire. Further, production of emissions other than CO_2 is often found to be highly correlated with these parameters. For example, see Figure 1 or the equation for the emission factor for CO as a function of CE in Ward et al (1992).

A series of extensive field measurements of fuel types, combustion efficiency, and other fire variables, by several workers, in tropical ecosystems in Brazil and Africa suggested a working, preliminary classification scheme for tropical fire-types (Ward et al 1992; 1996; Shea et al 1996). Typical fires during the peak of the burning season in savannas, partially-treed savannas, or cerrado were found to burn with a CE of 0.93 - 0.94 (MCE 0.94 - 0.95). In contrast, deforestation burns in primary moist forest burned with an average CE of 0.86 (MCE 0.89). In comparison to primary forest, fires in second-growth forest (smaller fuels than primary) burned with a higher average CE of 0.89 (MCE 0.91). Pastures, which often have large fuel elements left over from pre-existing forests, burned, on average, with an intermediate CE of 0.92 (MCE 0.934). The absolute values of CE obtained in an experiment (such as that described above) depend partly on the number of components measured and the measurement time (Hurst et al 1994). For differentiation of fire-types, the important result is that different parameter values are obtained for different fire-types within any consistent approach.

Our concept of a fire-type recognizes that the emissions (per unit area and time) for a land-cover type depends on the fire CE and also on the biomass density (Whitmore 1984), combustion factor (CF, the fraction of biomass exposed to fire that burns), and fire frequency (Shea et al 1996). In summary, land-cover types with low biomass density, such as grasslands, normally feature fires with high CE (~0.94), high CF (~1.0), and shorter (1-4 yr) "fire return intervals" (Kauffman et al 1994). Land-cover types with high biomass density, such as primary moist forest, typically feature fires with lower CE (~0.86), and lower CF (0.3-0.5). Intermediate values for CE and CF are appropriate for pastures and secondary forests. Within a land-cover type, the combustion factors are normally higher for the finer fuels (Fearnside et al 1993; Ward et al 1992; Shea et al 1996).

The premise of this paper is that emissions estimates, in general, and national greenhouse gas inventories, in particular, can be significantly improved by estimating the appropriate fire-types involved and then coupling that information to fire-type-specific emission factors.

Fire-Type Specific Emission Factors

This paper is not intended to be a complete review, or even a list, of all previous emissions measurements. The purpose is to describe the methodology for modeling emissions by fire-type and to refer the reader to the data needed to successfully apply this model.

Hydrocarbons. Figure 1 shows $EFCH_4$ (grams CH_4 per kilogram of dry fuel) *vs.* CE. Each data point represents integrated data from a field fire. The points are divided into two groups; one from forest and one from grassland ecosystems. A line is fit to the data for each group, which is then a "best-fit" model for $EFCH_4$ as a function of CE for that group of ecosystems. The vertical lines represent the average CE observed in Ward et al (1992) for two of the fire types. For example, cerrado fires (solid lines) typically burned with a fire-integrated CE of 0.94 and produced about 2 g CH_4/kg, while fires in primary forests (dashed lines) burned with lower CE and produced about 8 g CH_4/kg.

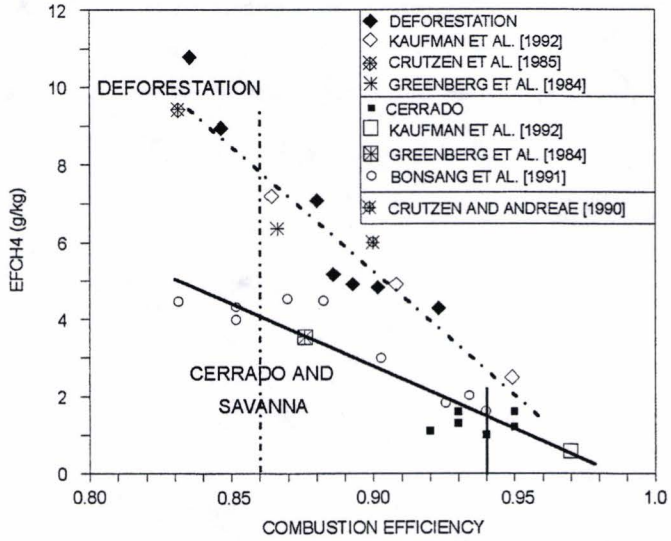

Figure 1. Methane production versus combustion efficiency shown for fires in grass-dominated and forested ecosystems (Ward et al. 1992).

The EF for non-methane hydrocarbons (NMHC's) can also be modeled as a function of CE or MCE. However, in Hao et al (1996), NMHC emissions were found to correlate better with CH_4 emissions and so *emission ratios* (ER) in the form NMHC/CH_4 are presented. Thus, NMHC EF's can be estimated by first determining the appropriate EFCH_4 and then applying the appropriate ER. In fact, much of the biomass burning literature presents emissions measurements as emission ratios to CO or CO_2 (Lobert et al 1991). Data in this form can be readily used in a fire-type specific model by first scaling CO and CO_2 appropriately and then applying the reported ER. The two step process will not generally give exactly the same result as the CE model, but should be preferred to ignoring fire-type. (In the special case of a very high CE fire for which very little data was obtained at high CE the two step process may be preferred. This is because a linear fit effectively weights the low CE points.) Finally, large amounts of terpenes may also be emitted in some fires (Yokelson et al 1996a; work in progress).

Oxygenated organic compounds (OVOC). Organic acids, alcohols, and aldehydes are not primarily created by the same process that produces CH_4 (Yokelson et al 1996b; 1997a). OVOC emission factors do not correlate well with CH_4 or MCE in most studies (Talbot et al 1988). However, in our open-path spectroscopic measurements, we obtain emission factors for OVOC which are 10 - 1000 times higher than other studies and *are* well-correlated with MCE. This is shown in Figure 2 for acetic acid where a single line is fit to spectroscopic measurements from grass, brush, and coniferous fuels. More study will be required to determine if fuel-specific slopes are appropriate.

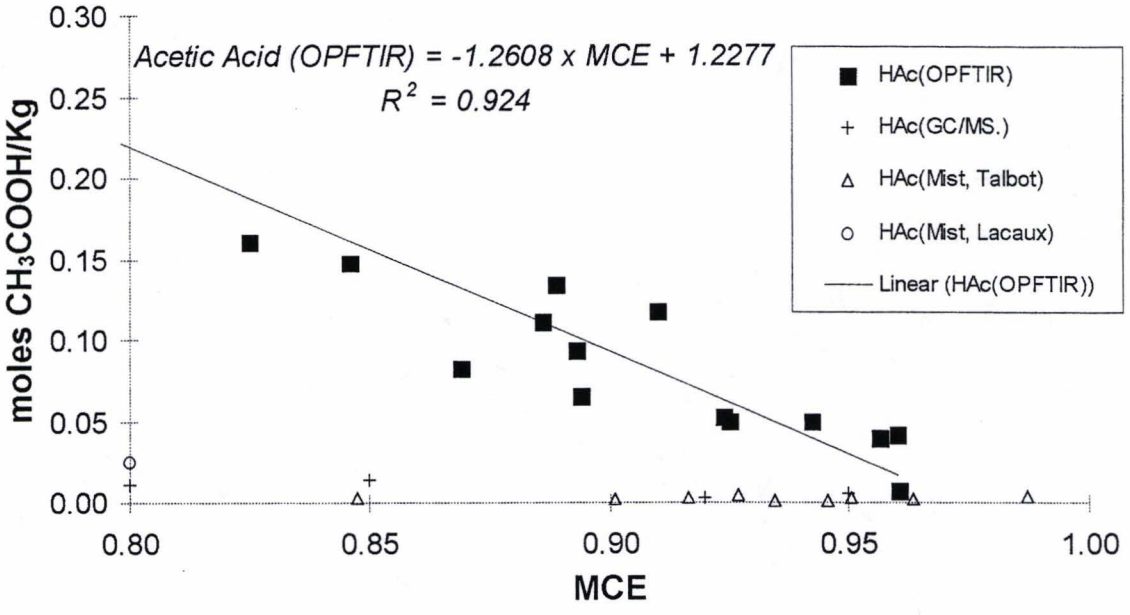

Figure 2. The line is fit to the open-path Fourier transform infrared spectrometer measurements of the Acetic acid emission factors for grass, brush, and coniferous fuels (Yokelson et al 1996b; 1997a). The EF is in moles/kg (MM CH_3COOH = 60 grams per mole).

Nitrogen compounds. Plots of EF *vs.* CE for N compounds often show poor correlation due to large variation in fuel N. One solution is to normalize EF to fuel N, but

fuel N is not always measured. We have developed another alternative which can effectively normalize key N emissions without requiring fuel N data as explained next (Yokelson et al 1996b). Several studies have quantified ammonia (from smoldering) and NO_x (from flaming) for fires primarily consuming aboveground biomass. Hurst et al (1994) measured the percentage of fuel nitrogen released as the sum "NH_3+NO_x" from Australian savanna fires and obtained 44%. Yokelson et al (1996b) obtained 54% for this quantity in laboratory studies of coniferous fuels. In both these studies, HCN, N_2O, and other compounds were minor products accounting for less than 1 % of fuel N. Many studies report that about 10 percent of fuel N remains in the ash (e.g. Hurst et al 1994; Crutzen and Andreae 1990). Finally, Kuhlbusch et al (1991) report that N_2 will account for 36 ± 13% of fuel N on average. The above observations can be combined with measurements of NH_3/NO_x from a variety of studies and the major nitrogen emissions (except for N_2) can then all be estimated within a single model. This approach is illustrated in Figure 3. NH_3 and NO_x are estimated as follows: 1. Fuel N can be measured or extensive tables of C, N, and H content in tropical fuels are available (Sussot et al 1996), 2. The approximation is made that 50% of the fuel N is released as NH_3 or NO_x, and 3. the ratio NH_3/NO_x (for the estimated fire MCE) is given by the equation in Figure 3.

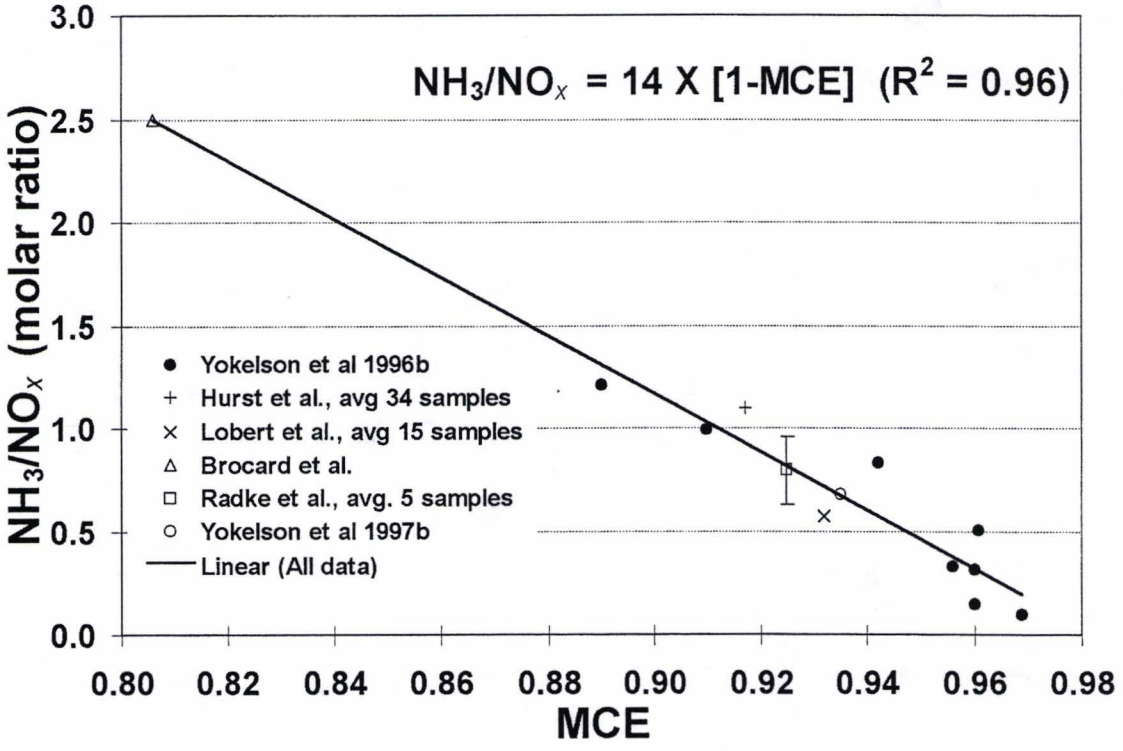

Figure 3. The data for NH_3/NO_x as a function of MCE, a linear fit to the data, and an equation to predict emissions are shown.

Hydrogen and Sulfur Compounds. The bulk of the fuel H can be accounted for fairly easily in the trace gas emissions. H_2O is the major flaming combustion product with the "combustion water" accounting for some 90% of fuel H (Yokelson et al unpublished work). H_2 is a major H-containing product of smoldering combustion (Crutzen et al 1979; Cofer et al 1988; 1990; Ward et al 1992) and substantial quantities of hydrogen are also

contained in the OVOC and hydrocarbons. It has been more difficult to account for fuel S in the emissions. Qualitatively SO_2 is identified with flaming (Yokelson et al 1996b) and OCS with smoldering (Crutzen et al 1979; 1985; Ward et al 1982; Yokelson et al 1997a).

Aerosols. The chemical composition and the initial production and growth mechanisms for aerosol emissions from biomass fires are still poorly characterized. Qualitatively, PM2.5 usually accounts for *ca.* 1% of the fuel carbon which is much less than the ~ 20 % soot yields sometimes reported from open fires in fossil fuels. (Biomass fire particulate also has much lower PAH content than particulate from fossil fuel combustion.) Some equations have been derived from ground-based measurements to predict EFPM2.5 as a function of CE:

(1) EFPM2.5 (g/kg) $\cong$ 88 X [1-CE] $r^2 = 0.56$

Equation 1 was determined from studies of savanna fires in Africa (Ward et al 1996).

(2) EFPM2.5 (g/kg) $\cong$ 70 X [1-CE] $r^2 = 0.59$

Equation (2) fits data from fires in the cerrado, and secondary and primary forest of Brazil (Ward et al 1992). Finally, equation (3) relates the observed particulate concentration to the excess CO concentration and has been verified downwind of biomass fires in both the tropics and temperate regions (Babbitt et al 1995).

(3) [PM2.5] (μg/m3) $\cong$ 100 X [CO] ppm

Flaming combustion is found to contribute strongly to black aerosol which may absorb significant amounts of solar radiation while smoldering combustion contributes strongly to a white, more reflective (higher albedo) aerosol (Susott et al 1991; Yokelson et al 1997a). Glowing combustion does not release visible aerosol, but the emissions contain NH_3 which is a precursor for secondary aerosol formation in the plume (Yokelson et al 1997a).

Belowground biomass. Globally, it has been estimated that over two-thirds of the carbon in forest ecosystems is contained in soils and peat deposits (Dixon et al 1994) and that carbon contained in soils represents a larger carbon pool than carbon in aboveground biomass (Woodwell et al 1978). Land-use change and global warming may cause more of this carbon to be exposed to fire (Kasischke et al 1995; Keane et al 1997). Organic soils and "litter" differ from aboveground fuels in that they burn almost exclusively by smoldering combustion. The general picture of emissions from soils can be predicted by referring to the "low CE" portion of the EF plots. However soils develop under many different physical, chemical, and fire regimes and from a large variety of biological and geological precursors. These factors may explain why our soil fire emissions database is apparently not well-described by simple relationships. For instance, in organic soils the HCN/NH_3 ratio varies about two orders of magnitude. HCN production is evidently higher in drier soils and actually dominated ammonia production by a factor of five for a fire in dry North Carolina bog soil (Yokelson et al 1997a). Finally, we measured the tar yield from smoldering peat at slightly over 1%. However, the tar was enriched in N by a factor of 6 or 7 over the parent peat, suggesting that the tar may account for a significant

portion of fuel N in soils. Table 1 presents the major emissions we detected from burning organic soils (Yokelson et al 1997a).

Table 1. Average of all emission data for smoldering organic soils. Adapted from Yokelson et al. 1997a.

compound name	formula	100 X moles compound / total moles C detected		Approx.[1] g/kg
carbon dioxide	CO_2	78.82	(3.593)[2]	1445
carbon monoxide	CO	17.10	(3.634)	200
methane	CH_4	1.220	(0.440)	8.13
ammonia	NH_3	0.932	(0.767)	6.60
acetic acid	CH_3COOH	0.306	(0.145)	7.65
hydrogen cyanide	HCN	0.292	(0.166)	3.29
methanol	CH_3OH	0.281	(0.100)	3.75
propene	C_3H_6	0.149	(0.027)	2.61
ethene	C_2H_4	0.140	(0.040)	1.63
formaldehyde	HCHO	0.132	(0.096)	1.65
phenol	C_6H_6O	0.107	(0.122)	4.19
formic acid	HCOOH	0.073	(0.060)	1.40
2-hydroxyethanal	$C_2H_4O_2$	0.032	(0.031)	0.80
carbonyl sulfide	OCS	0.021	(0.038)	0.53
ethyne	C_2H_2	0.013	(0.007)	0.14

[1]Calculated assuming fuel is 50% carbon.
[2]The value of one standard deviation is given in parentheses.

Secondary product formation. Most of the initial emissions from fires (except for CO_2 and CH_4) are too reactive to become well mixed in the global troposphere (Prather et al 1994). Photochemical processes transform the initial plume constituents into new products on the time scale of hours to months (Finlayson-Pitts and Pitts 1986). Of these secondary products, O_3 has attracted the most attention because of its importance as a pollutant, oxidant, and an indirect greenhouse gas. O_3 formation in biomass burning plumes has been the focus of major, international, collaborative measurement and modeling efforts which are only very briefly summarized here (Talbot et al 1996; Singh et al 1996; Fishman et al 1996; Yokelson et al 1997c). Fires initially cause a large reduction in the O_3 levels in entrained background air by reaction with NO and perhaps terpenes. Under the right conditions, O_3 can then increase to high levels in the plume over a period of weeks as discussed in detail elsewhere (Crutzen and Carmichael 1993; Thompson et al 1996). The model of Chatfield et al (1996) indicated that O_3 formation was "NO_x limited." This suggests that a high N:C ratio of the fuel coupled with a high fire CE may increase the O_3 formation potential of fires. These same fire-types may also have relatively large potential to contribute to acid rain and deposition. However, it is not yet possible to make a simple assignment of emission factors for secondary products from specific fire-types.

Conclusions

It is well established that different types of fires can produce significantly different emissions. Coupling this information with measurements of fire-types and amounts should improve regional-global emissions estimates. Future improvements will result from researching seasonal trends in fire-types and amount burned and from measurement of specific emission factors for more compounds and fires. Finally, detailed understanding of the influence of fires on the atmosphere will require integrated study of the post-emission transport and transformation of the trace gases and aerosols.

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